

Permittivity and transmission of metals

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Abstract: *Transmission measurements for both nanosphere solutions and various metal films on glass are performed. The results are then compared to theoretically calculated values. Also, the electron permittivity of the metal films is compared to the Drude model.*

Introduction

Thin films of silver and gold, with thickness smaller than the wavelength of light, are put on glass. When light strikes the surface of a film it is either transmitted or reflected. Transmission and reflection of the films can be calculated if the refractive index of the material is known. The refractive index here is a complex number, commonly denoted as $\hat{n} = n + ik$, where the imaginary part gives absorption of the material and the real part gives the phase speed. From this refractive index the electron permittivity can be determined.

Nanoparticles, or ultrafine particles, have a diameter between 1 and 100 nm. Nanoparticle research is currently a very interesting area because of a wide variety of potential applications in biomedical, optical and electronic fields. They are a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size. But at the nanoscale, properties dependent of size are often observed. That is the properties of materials change when their size approaches the nanoscale and the percentage of atoms at the surface of a material becomes significant. Nanoparticles are small enough to confine their electrons and produce quantum effects and therefore often possess unexpected optical properties. Gold nanoparticles appear deep red to black in a solution, they melt at much lower temperatures than gold slabs and the smaller the particles are the greater the solar absorption is.

Theory

The electron permittivity, ϵ_r , is the material's ability to transmit, or permit, an electric field. The electron permittivity for silver and gold can be calculated from

$$\epsilon_r = (n + ik)^2 \quad (1)$$

where the real part, n , is the refractive index and the imaginary part, k , indicates the amount of loss due to absorption when the electromagnetic wave propagates through the material. For gold both parts vary with wavelength, n_{Au} decreases and k_{Au} has an overall increase. For silver the refractive index is a constant, $n_{Ag}=0.045$, and k_{Ag} increases

with wavelength. The relation between ϵ_r and ϵ is

$$\epsilon = \epsilon_r \epsilon_0 \quad (2)$$

where ϵ_r is the relative permittivity of the material and ϵ_0 is the vacuum permittivity. The relative permittivity can be compared to the Drude model

$$\epsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (3)$$

where ω_p is the bulk plasma frequency and γ is the intraband damping term (inverse of the relaxation time τ). Experimentally determined values from M. G. Blaber et al^[2] used in the Drude model can be seen in table 1.

Table 1: Experimental determined values used in the Drude model.

Element	$\omega_p[eV]$	$\gamma[eV]$
Ag	9.6	0.0228
Au	8.55	0.0184

A Fabry-Pérot etalon is usually a transparent plate with two reflecting surfaces. Its transmission spectrum as a function of wavelength shows peaks of large transmission corresponding to resonance of the etalon. Interference between the multiple reflections of light between the two reflecting surfaces is the reason for the varying transmission function of the etalon. If the transmitted beams are in phase a constructive interference occurs which corresponds to a high transmission peak of the etalon. If the transmitted beams are not in phase, destructive interference occurs. This corresponds to a transmission minimum. The wavelength of the light, the angle it travels at through the etalon, the thickness of the etalon and the refractive index of the material between the reflecting surfaces determines whether the multiple reflected beams are in phase or not. A high finesse etalon shows sharper peaks and lower transmission minima than a low finesse etalon.

To complicate things the symmetry of etalon is broken with an addition of a thin film. Reflection and transmission of the film is typically followed with a change in phase while a simple junction, like etalon, gives a change in sign at most.

In this experiment one to three layers on a glass are observed.

When a particle's diameter d is much smaller than the wavelength of light in the surrounding medium, $d \ll \lambda$, the interaction of the particle

with the electromagnetic field can be analyzed using the simple quasi-static approximation. The phase of the harmonically oscillating electromagnetic field is practically constant over the particle volume, so the spatial field distribution can be calculated by assuming a particle in an electrostatic field. The harmonic time dependence can then be added to the solution once the field distributions are known. This is the lowest-order approximation of the full scattering problem and describes the optical properties of nanoparticles of dimensions below 100 nm for many purposes. The polarizability of a small sphere of sub-wavelength diameter in the electrostatic approximation is

$$\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \quad (4)$$

where a is the particle's radius, ϵ_m the dielectric constant of the isotropic and non-absorbing surrounding medium and ϵ the simple complex number taken for the dielectric function $\epsilon(\omega)$ which describes the dielectric response of the sphere. Resonance frequency (wavelength) is when α reaches its maximum value.

Experimental

In the setup an EQ-99 LDLS (Energetiq-99 Laser-Driven Light Sources) was used as a light source. The light source emits white light because it has a very high brightness across the visible spectrum. In front of the lamp is a filter to decrease the light intensity towards the sample. Behind the sample is another filter to focus the light to the spectrometer. This setup can be seen in fig. 1.

Transmission as a function of wavelength is measured for thin metal films. First a background measurement is made along with the spectrum from the light source. The setup and surroundings are kept unchanged while transmission measurements for various thin silver and gold films are made. The films measured were 15 nm and 30 nm thick silver films, two 15 nm silver films with a 670 nm thick plastic in between and 6 nm and 15 nm gold films. Because of irregular transmission activity for the 6 nm gold film, comparison measurements are made for gold nanospheres with diameters of 50 nm and 100 nm . Before this was done, new background measurements with a water-jacketed absorption cell were made. Then the particle solutions are added to the cell.

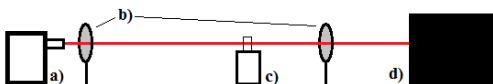


Fig. 1: Schematic experimental setup. a) Light source; b) filters; c) mounted sample; d) spectrometer.

A Matlab program was provided in order to calculate theoretical transmission of the metal films.

Calculations

In figs. 2 and 3 the relative electron permittivity for silver and gold is determined with eqs. (1) and (2) and compared to the Drude model, eq. (3).

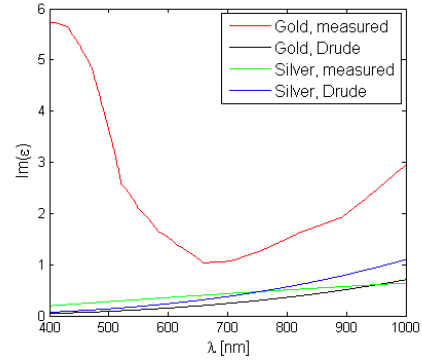


Fig. 2: $\Im(\epsilon)$ for both measurements and the Drude model.

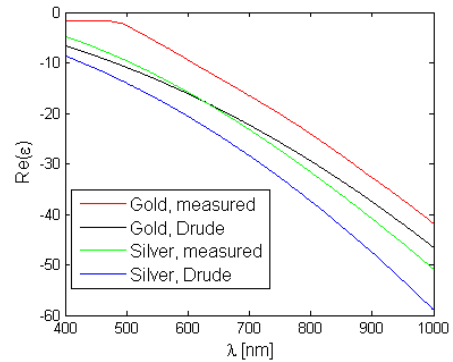


Fig. 3: $\Re(\epsilon)$ for both measurements and the Drude model.

Transmission for the three types of silver films on the glass is shown in fig. 4. The Matlab program was used to find the best match to the measured curves. A loss factor of $k=0.027$ for all wavelengths was added to the PMMA plastic in the calculations for a better coherence with measurements.

The transmission for the 6 nm and 15 nm gold films can be seen on fig. 5, along with the theoretical transmission calculated with the Matlab program.

Transmission for the 50 nm and 100 nm gold particles is shown in fig. 6 along with accurately calculated values for $20, 40$ and 80 nm gold particles acquired from P. K. Jain et al^[1]. The resonance wavelength for the particles are shown in table 2. Eq. (4) with the electron permittivity from eq. (1) is used to calculate the resonance wavelength for a small gold particle, $a \ll \lambda$, in various mediums. The results can be seen in table 3.

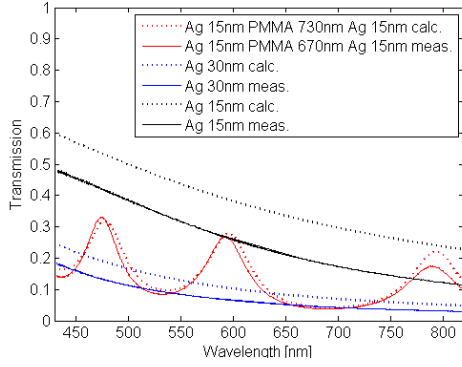


Fig. 4: Measured and calculated transmission as a function of wavelength for the silver films.

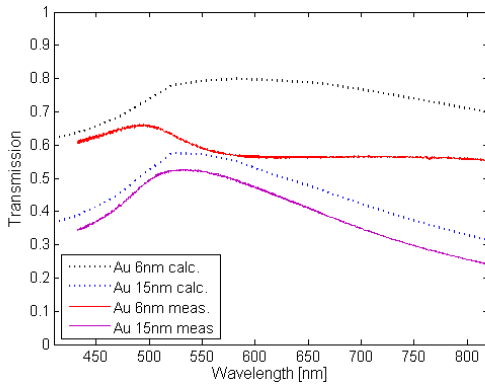


Fig. 5: Measured and calculated transmission as a function of wavelength for the two gold films.

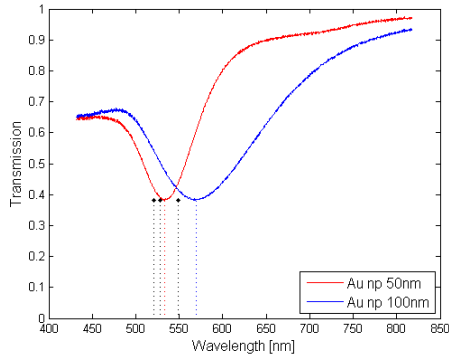


Fig. 6: Transmission as a function of wavelength for the gold nanoparticles. The dotted lines show the resonance freq. for nanospheres with different diameters from table 2.

Conclusion

As can be seen in figs. 2 and 3, the Drude model is relatively consistent with measured permittivity of silver and gold, except for $\Im(\epsilon)$ of gold, where the Drude model is by no means comparable to the measured value.

Transmission measurements of silver, seen in fig. 4, show that the PMMA plastic is probably thicker

Table 2: Resonance wavelength for the gold particles.

Diameter [nm]	Wavelength [nm]
20	521
40	528
50	534
80	549
100	569

Table 3: Resonance wavelengths for gold nanoparticles in various mediums.

Medium	Refr. index n	Res. wavelength [nm]
Air	1.0	536
Water	1.333	551
Glass	1.5	564

than expected. The PMMA thickness controls at what wavelengths the transmission peaks are, so a 730 nm thick PMMA is more likely than the expected 670 nm. Also, the plastic might have a curved surface, making the middle thicker than the edges, which might be the reason for this difference.

For the gold and silver films, figs. 4 and 5, the measured transmission is somewhat smaller than theoretically calculated. This can be caused by losses from the rugged surface of the glass and from the glass to air junction. These losses were not included in the calculations.

The 6 nm gold film from fig. 5 has an unexpected behaviour. The cause of this is because it is so thin that it starts behaving like individual particles instead of a solid film. The unexpected drop in transmission around 500 nm can to some extent be related to the transmission drop of the gold nanospheres from fig. 6.

The measurements of the gold nanoparticles fit in with values taken from P. K. Jain et al^[1] for 20, 40 and 80 nm particles.

References

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