Dielectric properties of ultrathin metal films around the percolation threshold

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We report on optical reflection measurements of thin Au films at and around the percolation threshold (film thickness 3 to 10 nm) in an extremely broad spectral range from 500 to 35 000 cm\(^{-1}\) (0.3 – 20 μm). Combining spectroscopic ellipsometry and Fourier-transform infrared spectroscopy, the dielectric properties of the films can be described over the whole frequency range by Kramers-Kronig consistent effective dielectric functions. The optical conductivity of the films is dominated by two contributions: by a Drude-component starting at the percolation threshold in the low frequency range and a plasmon in the near-infrared region, which shifts down in frequency with increasing film thickness. The interplay of both components leads to a dielectric anomaly in the infrared region with a maximum of the dielectric constant at the insulator-to-metal transition.

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I. INTRODUCTION

Although for many applications closed metal films as thin as possible are desired, the dielectric properties of percolating metal films around the insulator-to-metal transition are not well understood. Thick continuous metal films show a behavior similar to bulk material and can therefore be well described by the Drude-model when corrections for size effects are considered. With decreasing thickness, the films become granular, and below the percolation threshold the metallic behavior disappears as far as the electrical transport is concerned. In principle one can try to simulate semi-continuous metal films with effective medium (EMA) theories. However it was shown that EMA models fail to describe the dielectric properties of ultra-thin metal films. In general this transition region was not yet studied in detail over a broad frequency range; nevertheless, these investigations should eventually provide the data to link the abrupt change in dc-conductivity with the observed shift of plasmon resonances in the visible.

On the low frequency side of the electromagnetic spectrum, percolation theories deal with an “idealized” dc-conductivity or the electrical behavior at audio and radio frequencies up to some MHz. On the other side of the spectrum – in the visible and ultraviolet – a large number of investigations have been carried out to understand the optical properties of arrays of clusters at surfaces. In between, however – in the infrared and far-infrared spectral region – little has been done so far. Here we report on Fourier-transform infrared reflection spectroscopy and spectroscopic ellipsometry measurements of thin Au films on Si/SiO\(_2\) covering the infrared to ultraviolet spectral range between 500 to 35 000 cm\(^{-1}\) (60 meV to 4.3 eV), corresponding to a wavelength of 280 nm to 20 μm. The film thickness \(d\) was varied between 3 and 10 nm, i.e. from well below to well above the insulator-to-metal transition.

II. EXPERIMENTAL DETAILS

Thin Au films were prepared by an electron-beam heated effusion cell on clean 0.55 mm thick Si(100)-substrates covered by a 200 nm SiO\(_2\) layer. The substrates were polished on both sides and held at room temperature during evaporation. The preparation was performed in ultra high vacuum (UHV) at a base pressure of 1 \(\times\) 10\(^{-7}\) Pa. The deposition rate was about 1 Å/min and measured prior to each film-deposition by a quartz crystal microbalance. Keeping the gold-flux constant the film thickness could be controlled by the evaporation-time. The film thicknesses vary from \(d = 3.4\) nm to 9.5 nm.

All optical experiments were performed at room temperature. The reflectivity measurements in the infrared (IR) were carried out by a Bruker IFS 66/s Fourier transform infrared (FTIR) spectrometer in the range 500–12 000 cm\(^{-1}\) employing a nitrogen cooled mercury-cadmium-telluride (MCT) detector. All spectra were recorded with a resolution of 0.5 cm\(^{-1}\) and 64 averaged scans. As reference a thick gold mirror was used. To compare measured spectra with model calculations, etalon effects (multireflection within the substrate) were smoothed out. For the ellipsometry measurements a Woollam variable angle spectroscopic ellipsometer (VASE) was utilized. The experiments were carried out in the spectral range between 6000 and 35 000 cm\(^{-1}\) (0.75 to 4.3 eV, corresponding to a wavelength of 280 nm to 1.7 μm) with a resolution of 170 cm\(^{-1}\) and an angle of incidence varied in steps of 5° from 35° to 75°.

III. RESULTS AND ANALYSIS

The thickness dependent morphology of thin Au-films on Si/SiO\(_2\) is well investigated. In Fig. atomic force microscopy (AFM) images at the same scale from a former investigation of 3 nm, 5 nm, and 7 nm thick gold films are presented.
With increasing film-thickness the size of the islands increases, they get closer to each other and the films become smoother. The root-mean-square roughness of the 3 nm film is about 1 nm, and the average cluster size is about 4 nm. The percolation threshold itself cannot be determined from the morphology. Although it is important to know the morphology of the films, one has to stress the fact that percolation theories deal with scaling laws and therefore the overall electrical and optical behavior should be independent of the specific morphology.

Prior to the film preparation, the bare Si/SiO\(_2\) substrates were characterized by ellipsometry and the obtained optical parameters then kept constant in the further modeling of the films. As an example, in Fig. 2 the measured ellipsometric angle \(\Psi\) for a 8.1 nm thick Au film is shown as a function of frequency and angle of incidence. Several attempts were made to model the obtained ellipsometric angles: It was not possible, for instance, to model the granular films by an effective medium approximation (EMA), even in the case where the volume fraction was gradually decreased over the film thickness. Taking the granular Au layer as a homogeneous effective layer with fixed thickness, it was possible to get reasonable agreement to the experimental data by a point-by-point fit with MSE-values around 6; but it turned out that the received dielectric functions were not Kramers-Kronig consistent.

To solve this problem, we combined the results obtained by ellipsometry and IR-reflectivity. Both sets of data were simultaneously analyzed with the program package RefFIT. For details on this tool see Ref. 10. By means of a variational dielectric fit within the program, Kramers-Kronig consistent dielectric functions could be obtained, which perfectly reproduces both the ellipsometric angles (continuous line in Fig. 2) as well as the IR-reflectivity. In Fig. 3 for example, the measured reflectivity in the IR-region (dashed line) of a 6.5 nm thick Au film with its corresponding fit (solid line) is shown together with an extrapolation to the ultraviolet obtained from the ellipsometric measurement. The dominating oscillation in the reflectivity is due to interferences caused by the 200 nm thick SiO\(_2\) layer.

The real part \(\epsilon_1(\omega)\) of the dielectric function as received from the above analysis is shown in Fig. 4 as a function of frequency for varying film thickness. From the imaginary part \(\epsilon_2(\omega)\) the optical conductivity \(\sigma_1(\omega)\) was calculated by:

\[
\sigma_1(\omega) = \omega \varepsilon_0 \epsilon_2(\omega),
\]

with \(\varepsilon_0\) the permittivity of free space. It is displayed in Fig. 5 in a double logarithmic fashion.

The dielectric functions \(\sigma_1(\omega)\) and \(\epsilon_1(\omega)\) are described by a superposition of Drude- and Lorentz-terms. The
and the granular films with

d

The continuous films in the thickness range

\( d \)

the different films can be clearly divided in two regimes:

\( \varepsilon \)

the effective dielectric function

parameters obtained from the fits for the different film

changes at low frequencies.

\( d \)

threshold

between 6.5 and 7.0 nm where the sign in the slope of

\( \sigma \)

different thickness as indicated. The percolation occurs be-

FIG. 4: (Color online) The effective dielectric constant of

the gold films. Note the non-monotonous behavior at low

frequencies as the film thickness \( d \) increases (indicated by the

arrow). From a gold-film thickness of 8.1 nm on \( \varepsilon_1(\omega \rightarrow 0) \) is

negative, indicating the metallic behavior of the films.

parameters obtained from the fits for the different film

thicknesses are listed in Table II.

FIG. 5: (Color online) Optical conductivity of gold films of
different thickness as indicated. The percolation occurs be-

between 6.5 and 7.0 nm where the sign in the slope of \( \sigma_1(\omega) \)
changes at low frequencies.

IV. DISCUSSION

A. Perculation threshold

From the effective conductivity \( \sigma_1(\omega) \) as well as from
the effective dielectric function \( \varepsilon_1(\omega) \) of the gold layers,
the different films can be clearly divided in two regimes:

The continuous films in the thickness range \( d \geq 7 \) nm and the granular films with \( d \leq 6.0 \) nm. The percolation
threshold \( d_c \) falls right between these two values.

Well above the percolation threshold, the conductivity
depends on the low-frequency permittivity is concerned, one would expect that \( \varepsilon_1 \), which is positive for \( d = 0 \), gradually decreases with \( d \) and
becomes negative at the MIT. However, a distinctively
different behavior is observed in our experiments. As
indicated by the arrow in Fig. 4, \( \varepsilon_1(\omega) \) first rises with film
thickness \( d \), goes through a maximum at some critical
concentration \( d_c \) which is assumed to be around 6.0 nm, and
then decreases rapidly; \( \varepsilon_1 \) becomes negative only at
considerably larger \( d \) above 7 nm.

In principle, this behavior is known from the low-
frequency conductivity of percolating networks. Efros
and Shklovskii investigated such systems theoretically
and predicted a divergence of the static dielectric con-
stant

\[
\varepsilon_1(0, d) \propto (d_c - d)^{-s}
\]

at a critical thickness \( d_c \). For any small but finite fre-
TABLE I: The Drude- and Lorentz-parameters obtained from the fit to the model. The plasma frequency is denoted by \( \omega_p \) and \( \gamma = 1/(2\pi c\tau) \) is the scattering rate with \( c \) the speed of light and \( \tau \) the relaxation time. The bulk values are taken from Ref. 1.

| Film thickness | Drude | 1st Lorentz-oscillator | 2nd Lorentz-oscillator |
|---------------|-------|------------------------|------------------------|
| \( d \) (nm) | \( \omega_p/2\pi c \) (\(10^4 \) cm\(^{-1}\)) | \( \gamma \) (cm\(^{-1}\)) | \( \omega_0/2\pi c \) (cm\(^{-1}\)) | \( \gamma \) (cm\(^{-1}\)) | \( \omega_0/2\pi c \) (cm\(^{-1}\)) | \( \gamma \) (cm\(^{-1}\)) |
| bulk         | 7.27  | 210                    | –                      | –                      | –                      | –                      |
| 9.5          | 5.98  | 795                    | 7218                   | 2.96                   | 5210                   | 10480                  | 2.76                   | 4960                   |
| 9.0          | 4.70  | 1710                   | 6540                   | 3.60                   | 5920                   | 10400                  | 3.57                   | 4840                   |
| 8.1          | 4.79  | 3770                   | 8280                   | 3.27                   | 5290                   | 11500                  | 3.18                   | 4230                   |
| 7.0          | 3.23  | 5410                   | 7520                   | 3.71                   | 7090                   | 12220                  | 4.01                   | 5010                   |
| 6.5          | –     | –                      | 6940                   | 3.86                   | 8280                   | 12710                  | 4.23                   | 5740                   |
| 5.3          | –     | –                      | 9040                   | 3.27                   | 8540                   | 13620                  | 4.08                   | 5370                   |
| 4.5          | –     | –                      | –                      | –                      | 15650                  | 3.99                   | 5340                   |
| 3.4          | –     | –                      | –                      | –                      | –                      | 15600                  | 4.01                   | 5610                   |

FIG. 6: (Color online) Divergence of the dielectric constant at 1000 cm\(^{-1}\). The solid line is a fit to the data: \( \epsilon_1 \propto (6 - d)^{-1.3} \) for \( d < 6 \) nm and linear above. The dashed lines represent the predicted maximum after Eq. 3 for two and three dimensions.

For a more accurate analysis directly at the percolation threshold and a quantitative prove of equation (3), additional data with closer steps in thickness are required. It is interesting to note that the 7 nm film still exhibits a positive \( \epsilon_1 \) (cf. Fig. 4) albeit it possesses a Drude component.

C. Plasmons

For the description of the behavior at higher frequencies additional Lorentz-oscillators have to be considered. To illustrate how the conductivity is built up by the different components, the conductivity of the 9 nm film is shown in Fig. 7 together with its different contributions. With increasing film thickness the two oscillators shift to lower frequencies, become weaker and narrower (cf. Table I). In the following we will first concentrate on the second oscillator at higher frequencies which is caused by the ensemble of single particles. It is a property of the ensemble and has to be distinguished from free electron oscillations in single metal clusters. The incident electric field is modified by the polarizability of these particles which – most important – interact. In literature this transverse-mode plasmon is referred to as “Maxwell-Garnett resonance” or “optical conduction resonance”. It shifts to lower frequencies upon stronger interaction as the metal-islands become closer and denser packed. Assuming spherical clusters with a diameter much smaller than the used infrared wavelength, the position of this plasma absorption can be described by the following condition:

\[
\epsilon_1^{\text{bulk}}(\omega) = \epsilon_1 = \frac{2 + Q}{1 - Q a_s^2}.
\]
In this condition, \( Q \) is the area fraction of the substrate covered by metal, \( n_s \) is the refractive index of the substrate and \( \varepsilon_1^{\text{bulk}}(\omega) \) is the frequency dependent dielectric constant of the metallic fraction. For a given \( Q \), we can calculate the right-hand side of the equation and obtain a certain dielectric constant \( \varepsilon_1 \). The frequency at which the obtained resonance condition \( \varepsilon_1^{\text{bulk}}(\omega) = \varepsilon_1 \) is fulfilled gives the position at which the plasmon appears.

If we use the frequency dependent values \( \varepsilon_1^{\text{bulk}}(\omega) \) of bulk gold as calculated from and set \( n_s = 1.45 \) for the SiO\(_2\)-substrate, we get the solid line in Fig. 8. We can now compare this line with the measured plasmon frequencies in dependence of film thickness as listed in Table I as second Lorentz-oscillator \( \omega_0 \). Here we assume a linear relation between the film thickness \( d \) and the area fraction \( Q \) covered by the metal. As seen from Fig. 8 the plasmon shifts to lower frequencies with increasing film thickness \( d \), nicely following the behavior given by Eq. 4.

A closer inspection yields small deviations of the measured plasmon frequencies to lower values, which we ascribe to the influence of the substrate. The optical properties of the 200 nm oxide layer might be influenced by the underlaying silicon, which has a much higher refractive index. Taking a somewhat larger \( n_s \) in Eq. 4 shifts the calculated values to lower frequencies, i.e. closer to the experimental data.

As can be seen from Fig. 8 for \( Q \to 1 \) the calculated plasmon frequency shifts to zero and thereby mutates to a Drude-peak. It is known that the Maxwell-Garnett theory breaks down above the percolation threshold, which in our case is at about \( Q = 0.6 \), therefore the extrapolation to \( Q \to 1 \) is disputable. Nevertheless, the experimentally found position of this plasmon can still be described quite well within this theory even above the percolation threshold (see Fig 8).

Recently de Vries et al. interpreted their ellipsometric measurements on thin silver films in the visible and near-infrared spectrum exactly in this way: the resonance frequency of a localized plasmon shifts to lower frequencies with increasing film thickness becoming zero at the percolation threshold. There the relaxation time exhibits an abrupt increase indicating the transition to a macroscopic conducting state.

Our measurements, which extent to the far infrared, reveal a different picture. At the percolation threshold we can clearly see both the development of a Drude-peak and the presence of the plasmon. Even well above the percolation threshold, the position of this plasmon can still be described satisfactorily by Eq. 4, but it gradually dies out with increasing film thickness \( d \). This can in principle be interpreted in the way that the rough surface of the percolated films still show dipole interaction or that dielectric inclusions in the film start to interact with each other, as it has been considered by Cohen et al. In a direct comparison of the conductivity of the calculated and measured plasmon the Lorentzian-line of the latter one is broadened (data are not shown). This comes from the fact that the particle size is smaller than the mean free path of the conduction electrons. As seen before, this size effect also leads to a large scattering rate in the Drude component of the percolated films (cf. Table I). Therefore the Maxwell-Garnett theory gives correctly the resonance position but the calculated plasmon band is wider than expected. The occurrence of this effect for thin films was already predicted by Doremus.

As discussed above the plasmon referred to as second
FIG. 9: Spectral weight and electron density $N_e$ of the Drude- and the two Lorentz-oscillators as function of the film thickness. The dashed line represents the electron density as determined for bulk gold.

Lorentz oscillator in Table I is a property of an ensemble of single clusters. At low coverage only this peak is seen. At higher coverage a second peak at lower frequencies appears. This mode is an indication for the formation of aggregates. At low coverage only this peak is seen. At higher coverage a second peak at lower frequencies appears. This mode is an indication for the formation of aggregates. At low coverage only this peak is seen. At higher coverage a second peak at lower frequencies appears. This mode is an indication for the formation of aggregates.

As frequency increases both plasmon peaks shift to lower frequencies, they broaden and the splitting between them increases. In the classification given by Kreibig et al. the sample undergoes a transition form category II (separated single clusters in full statistical disorder) to category IV (various kinds of aggregates, various next neighbor distances, plus single particles). At the percolation threshold, when additionally the Drude component appears, they can not be clearly separated anymore (see Fig. 9).

The maximum in $\epsilon_1(\omega)$ at the critical thickness at low frequencies is now a direct consequence of the two competing contributions: below the percolation threshold the shift of the plasmons towards lower frequencies with increasing film thickness leads to an increasing $\epsilon_1(\omega)$. At the percolation threshold $d_c$, the Drude-peak starts to develop, which adds a strong negative component to the dielectric response leading to a maximum in the dielectric function. Eventually $\epsilon_1$ changes sign at $d_0$, which is slightly above $d_c$. This interpretation is supported by the analysis of the spectral weight and the corresponding electron density $N_e$ shown in Fig. 9. The spectral weight increases linearly with film thickness reaching the bulk value at about 10 nm. No indication of the MIT between 6.0 nm and 7 nm can be identified, i.e. the abrupt change in dc-conductivity is not reflected at higher frequencies. There a monotonic transfer of spectral weight from the plasmons to the Drude-peak is observed. The linear increase of the electron density simply describes the growing amount of metal. A similar result for thin silver films was observed by de Vries et al.22.

V. CONCLUSION

Combining FTIR spectroscopy and spectroscopic ellipsometry the effective dielectric function of thin Au films around the percolation threshold could be obtained over a very broad frequency range from the infrared up to the UV. The optical properties of the films can in principle be described by two contributions: a plasmon in the near-infrared, which shifts down with increasing film thickness and than slowly dies out above the MIT, and a Drude peak, which starts to develop at the MIT and than rapidly increases with film thickness. The interplay of both components leads to a dielectric anomaly, known from percolation theory: from dc up to a few thousand wavenumbers $\epsilon_1(\omega)$ exhibits a pronounced maximum at some critical thickness.

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