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A new simple method of determining the effective mass of an electron or the thickness of thin metal films

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Abstract. A simple method of determining the effective mass m^* of free electrons in thin metal films (or the film thickness) only from the measured transmission of light in the range of the plasma reflection is discussed. The method is verified for gold films with thicknesses ranging from 7–40 nm. It was stated that the effective mass in this material does not depend on the film thickness and equals $(1.0 \pm 0.03)\, m_e$. On the other hand, knowing the value of m^*, the absolute film thickness can be obtained directly with a high accuracy within an error of a few ångströms, which is better than by the α-step or the Tolansky method.

1. Introduction

The effective mass m^* of an electron in thin metal films (for example, Ag, Au, Cu) is usually evaluated from the measured transmission and reflection spectra in the range of the plasma reflection. The relations for the transmission T and the reflection R may be solved numerically with respect to the real (ε_1) and imaginary parts (ε_2) of the dielectric constant. Under the Drude model one can write (for $(\omega\tau)^2 \gg 1$; τ is the relaxation time)

$$\varepsilon_1 \simeq \varepsilon_l - \omega_p^2/\omega^2 \qquad \omega\varepsilon_2 \simeq \omega_p^2/\omega^2\tau \tag{1}$$

where ε_l is the residual dielectric constant and $\omega_p^2 = Ne^2/\varepsilon_0 m^*$ the plasma frequency with N the electron concentration and ε_0 the permittivity of free space. Then, from the slope of the straight line when plotting the quantity ε_1 against $1/\omega^2$, the effective mass may be obtained.

In this method the absolute values of T and R as functions of energy must be known. Unfortunately, as was shown in [1], a relatively small error in the measured transmittance and reflectance may lead to a large error in the ε_1 and ε_2 values calculated in this way, and thus, in the computed value of m^*, as well. From the experimental point of view the transmission can be measured with a much better accuracy than the reflection. Moreover, the reflection is strongly influenced by different surface effects such as the surface roughness, oxidation etc.

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In the following we show how the effective mass or the film thickness d may be easily calculated from only the measured transmittance in the range of the plasma reflection.

2. Theory

The transmission coefficient T for a film on a transparent substrate may be written as

$$T = \frac{(1-R_1)(1-R_2)(1-R_3)\eta[1+(\kappa/n)^2]}{[1-2(R_1R_2)^{1/2}\eta\cos(\varphi_0+\varphi_1+\varphi_3)+R_1R_2\eta^2](1-R_3R'')}. \tag{2}$$

where

$$R_1 = \frac{(1-n)^2+\kappa^2}{(1+n)^2+\kappa^2} \qquad R_2 = \frac{(n-n_3)^2+\kappa^2}{(n+n_3)^2+\kappa^2} \qquad R_3 = \frac{(n_3-1)^2}{(n_3+1)^2}$$

$\eta = \exp(-2\kappa d\omega/c)$, c is the velocity of light in vacuum, d is the film thickness, n-iκ is the refractive index of the film and n_3 that of the substrate, $\varphi_0 = -2nd\omega/c$, $\varphi_1 = \tan^{-1}[2\kappa/(1-n^2-\kappa^2)]$, $\varphi_3 = \tan^{-1}[2\kappa n_3/(n_3^2-n^2-\kappa^2)]$. R'' is the reflection coefficient of the film measured in the semi-infinite substrate. Because R'' is very high in noble metals the factor $(1-R_3)/(1-R_3R'')$ in (2) may be replaced by unity.

In the plasma absorption range where $\omega^2\tau^2 \gg 1$ is valid the real and the imaginary parts of the refractive index may be written as

$$n \simeq \frac{\varepsilon_2}{(|\varepsilon_1|)^{1/2}} \simeq \frac{1}{2}\frac{\omega_p}{\omega^2\tau} \qquad \kappa \simeq (|\varepsilon_1|)^{1/2} \simeq \left(\frac{\omega_p^2}{\omega^2}-\varepsilon_1\right)^{1/2}. \tag{3}$$

For metals for which in the range of the plasma reflection the inequality $n \ll \kappa$ is valid the transmission is principally conditioned by the extinction coefficient κ. Thus, bearing in mind relation (3), we should expect that from the measured transmittance the effective mass, m^*, may be well estimated.

Assuming $\kappa^2 \gg 1$ and $(\kappa/n)^2 \gg 1$ one obtains from (2) as a good approximation:

$$\frac{1}{T} = \frac{[1-(R_1R_2)^{1/2}\eta']^2}{16n_3\eta'}\left(1+\frac{1+n_3}{\omega_p\tau}\right)\frac{\omega_p^2}{\omega^2}+C = \frac{S}{(\hbar\omega)^2}+C. \tag{4}$$

Here $\eta' = \exp(-2d\omega_p/c)$ and C is a complicated function of d, ε_1, ω_p, τ and n_3 but is practically independent from the energy. The term $(1+n_3)/\omega_p\tau$ is much less than one and, in practice, we can assume τ to be the same as in a monocrystalline sample (for Au: $\omega_p\tau \simeq 300$). The error in S caused by this assumption is less than 1%.

Expression (4) represents the equation of a straight line. From the slope S of this line and knowing the thickness of the film the plasma energy may be immediately obtained and then, assuming the electron concentration to be given, the effective mass m^*.

On the other hand, when $\hbar\omega_p$ is known the film thickness d may be calculated with high accuracy.

Figure 1 shows a plot of $1/T$ against $1/(\hbar\omega)^2$ for a hypothetical gold film with different thicknesses calculated from (2). One can see that in the energy region considered relation (4) with energy-independent C is excellently fulfilled. The assumed other parameter values in equation (2) and the values of $\hbar\omega_{pcal}$ obtained from the slopes of these straight lines are given in table 1. In table 1 'th' labels the values assumed in relation (2) when calculating T. The quantity $(R_1R_2)^{1/2}$ was assumed to be 0.99 which is a good approximation for Au films in the energy region considered. One can see from column

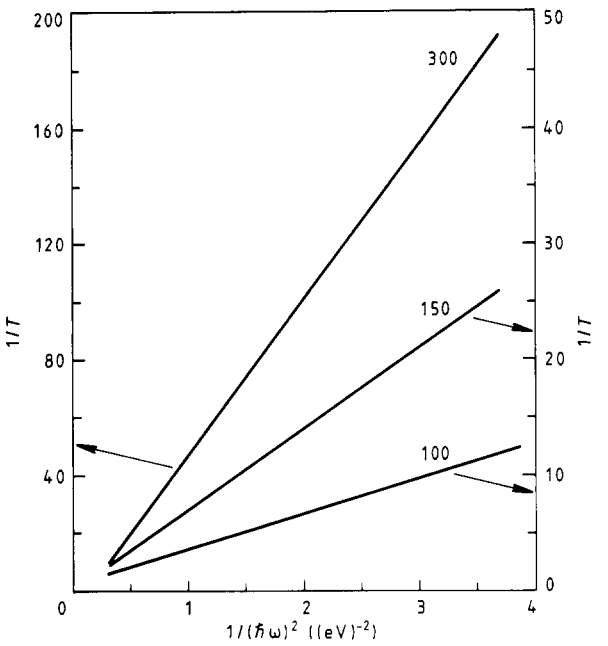

Figure 1. $1/T$ plotted against $1/(\hbar\omega)^2$ for hypothetical gold films with different thicknesses d given on lines in ångströms. The parameters for the calculation with (2) are given in table 1.

7 that the relative difference between $\hbar\omega_{pth}$ and $\hbar\omega_{pcal}$ is less than 1%. Further theoretical calculations have shown that effects such as polycrystallinity, surface roughness or the anomalous skin effect have only a small influence on the transmission spectrum and, therefore, on the slope of the straight line considered.

The polycrystallinity increases the slope of (4) and then the value of $\hbar\omega_p$. As an example some results obtained from (4) for hypothetical gold films with $d = 10$ nm (see table 1), grain diameter $D = 10$ nm and different reflection coefficients R_g of an electron at the grain boundaries are given in table 2.

The calculation was made using the relation for T given in [2] where the influence of the polycrystallinity on the optical properties is discussed. It is worth noting that the experimental values of R_g obtained from the DC conductivity are mostly about 0.3 [3, 4]. In such a case the error of $\hbar\omega_p$ calculated from (4) is about 1%. This fact was stated experimentally in our laboratory. For example, the measured transmittance of a film at

Table 1. The parameter values assumed in equation (2) and values of $\hbar\omega_{pcal}$ calculated from (4).

No	d (nm)	τ_{th} (10^{-14} s)	ε_{1th}	$\hbar\omega_{pth}$ (eV)	$\hbar\omega_{pcal}$ (eV)	$\Delta\hbar\omega_p/\hbar\omega_p$ (%)
1	10	2.15	8.2	9.017	8.98	−0.4
2	15	1.2	8.2	8.90	8.85	−0.6
3	30	1.0	8.0	9.33	9.38	0.5

Table 2. Values obtained for $\hbar\omega_p$ when including the grain boundary scattering.

R_g	0	0.1	0.2	0.3	0.4
$\hbar\omega_p$ (eV)	8.985	9.030	9.064	9.114	9.166

room temperature before and after annealing was nearly the same (maximum difference 0.25% in the energy range 0.4–2.0 eV) although the mean crystallite size was raised from 17 nm to 65 nm.

The surface roughness decreases the $\hbar\omega_p$ values calculated from (4). For films with $d = 15$ nm (see table 1) and an RMS value for the amplitude of the irregularities, $\sigma = 4$ nm, the value of $\hbar\omega_p$ is lowered of about 1%. The calculation is based on the relations given in [5].

It is worth noting that because the polycrystallinity increases and the roughness decreases the calculated value of $\hbar\omega_p$ one can expect the influence of these two effects to be partly cancelled in practice.

The influence of the anomalous skin effect on the slope of (4) was also examined and it turned out to be negligible [6]. For a film with $d = 10$ nm (see table 1) the maximum change of $\hbar\omega_p$ is less than 1%.

3. Experiment

Thin films of gold were prepared by vacuum deposition onto quartz (infrasil) or glass substrates with refractive indices in the infrared region of 1.448 or 1.515, respectively. To achieve very thin and continuous films (i.e. without holes) some substrates were pre-evaporated with a 0.2 nm thick chromium layer. The temperature of the substrates during the deposition was 300 K. The evaporation was carried out at a pressure of 1×10^{-4} Pa and the evaporation rate was of about 0.4 Å s^{-1}. The film thicknesses were monitored by a quartz oscillator. To obtain the true evaporation ratio a thick film was prepared and then measured by means of an alpha step at many different positions. For the gauge factor we obtained 10.6 ± 0.3 Hz $Å^{-1}$. The electron microscope analysis showed that all films were continuous and polycrystalline. The optical transmission measurements were performed with unpolarised light at normal incidence and at room temperature using a Beckmann Acta M IV UV/VIS/NIR double-beam spectrophotometer.

4. Results and discussion

In figures 2 and 3 the plots of experimental measurements are shown for gold films with different thicknesses d. One can see that relation (4) is very well fulfilled in the range 0.5–1.5 eV. The values obtained for $\hbar\omega_p$ and the effective mass m^* are given in table 3. In the framework of the experimental error of d ($\pm 3\%$) the m^* values of m^* agree well with the free-electron mass m_e independently of the film thickness. The average values obtained for m^* and $\hbar\omega_p$ are 1.01 and 8.98, respectively. Thus, finally, we can write

$$\hbar\omega_p = 9.0 \pm 0.13 \text{ eV} \quad \text{and} \quad m^* = (1.0 \pm 0.03)m_e.$$

Thin gold films have been extensively studied, so it is interesting to compare our results

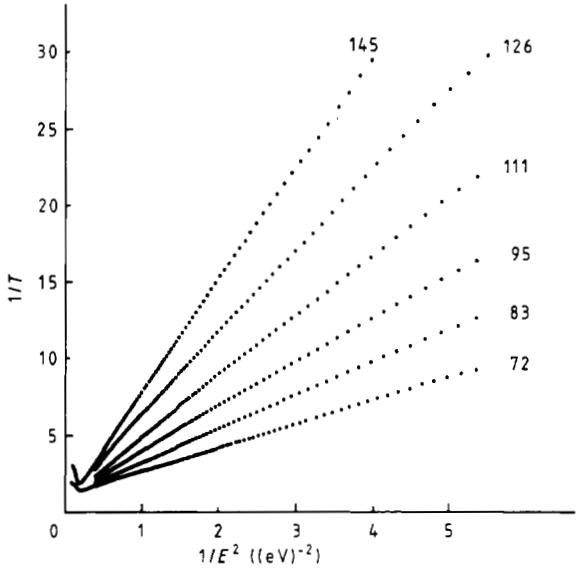

Figure 2. Adequate plots of the experimental measured spectra of different thin gold samples (with thicknesses given on lines in ångströms) deposited on quartz substrates ($n_3 = 1.448$).

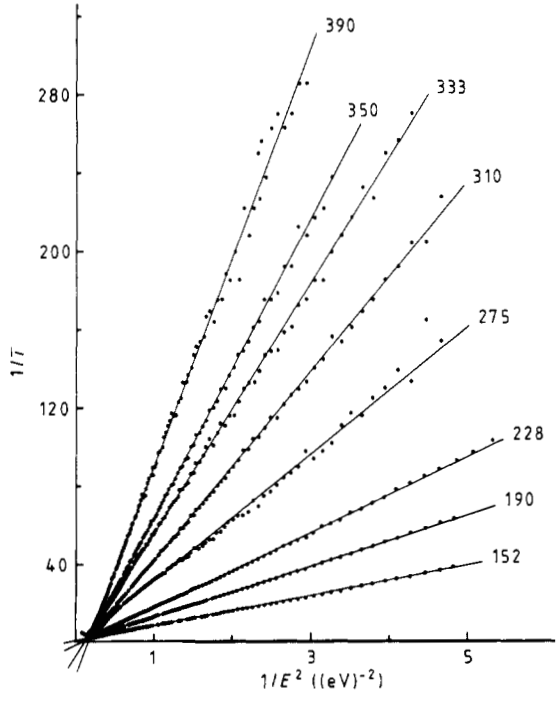

Figure 3. Adequate plots of the experimental spectra of different thin gold samples (with thicknesses given on lines in ångströms) deposited on glass substrates ($n_3 = 1.515$).

Table 3. Values of $\hbar\omega_p$ and the effective mass m^* for thin gold films.

d(Å)	S(eV^2)	$\hbar\omega_p$(eV)	m^*/m_e
$n_3 = 1.448$			
72	1.54	8.88	1.037
83	2.20	9.00	1.004
95	2.92	9.01	1.002
95	2.90	8.99	1.006
111	4.008	8.985	1.007
126	5.407	9.139	0.995
145	7.387	9.137	0.995
$n_3 = 1.515$			
53	1.07	9.00	1.00
134	5.697	8.959	1.014
152	7.80	9.024	0.999
171	9.91	8.953	1.015
190	13.096	9.004	1.004
208	16.38	8.998	1.005
228	19.20	8.844	1.04
275	33.214	8.898	1.027
333	65.00	9.029	0.998
389	107.75	8.958	1.014

with those reported in the literature. The reported values of the effective electron mass range from 0.94 m_e to 1.06 m_e [7]. Our results lie within this region.

Assuming the effective mass to be known (for gold we set $m^* = m_e$) and using relation (4) the film thickness may be obtained with high accuracy, i.e. to about a few ångströms. From (4) we obtain

$$d = \frac{\hbar c}{2\hbar\omega_p} \ln\left\{\frac{1}{(R_1R_2)^{1/2}} + \frac{8n_3S}{R_1R_2\hbar^2\omega_p^2} - \left[\left(\frac{1}{(R_1R_2)^{1/2}} + \frac{8n_3S}{R_1R_2\hbar^2\omega_p^2}\right)^2 - \frac{1}{R_1R_2}\right]^{1/2}\right\}^{-1}$$

and for Au

$$d \simeq 10.95 \ln\{1.01 + 0.1n_3S - [(1.01 + 0.1n_3S)^2 - 1.02]^{1/2}\}^{-1} \text{ (nm)} \tag{5}$$

where S is the slope in (eV)^2.

The error of the discussed quantities (m^* or d) may be estimated from an approximate relation

$$2(n_3S)^{1/2} \simeq \hbar\omega_p \sinh(\omega_p d/c)$$

and for $\omega_p d/c \leqslant 1$ one has

$$\frac{\Delta m^*}{m^*} \simeq \pm\left(0.5\left|\frac{\Delta S}{S}\right| + \left|\frac{\Delta d}{d}\right|\right). \tag{6}$$

The theoretical relationship between $\Delta m^*/m^*$ and $\Delta d/d$ for a hypothetical Au film with $d = 22$ nm ($\omega_p d/c \simeq 1$) is shown in figure 4. One can see that the deviation of this plot from (6) for $\Delta d/d$ small is negligible. The uncertainty in the slope $\Delta S/S$ is caused by the experimental error in the measured transmittance. However, the linear regression used to calculate S minimises the error so, in practice, $\Delta S/S$ is less than 1%. The much larger error in the estimation of m^* by the proposed method is caused by the uncertainty of the

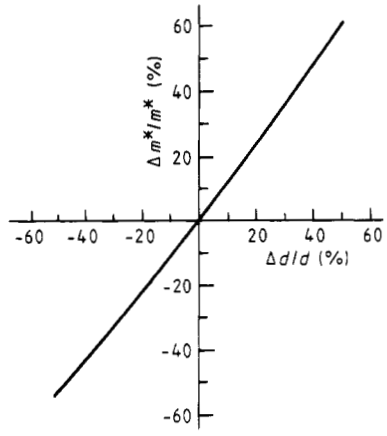

Figure 4. Relationship between $\Delta m^*/m^*$ and $\Delta d/d$ for a 22 nm thick gold film (relation (5)).

film thickness and one can set $|\Delta m^*/m| \simeq \Delta d/d|$. In our experiment $\Delta d/d$ was of about 3%.

The accuracy of estimating the film thickness d would be very high if the effective mass m^* were known. Unfortunately, for metals such as Au, Ag and Cu the value of m^* is known up to a few per cent which determines the uncertainty of the calculated thickness. In spite of this the relative accuracy of the estimate of d, which does not depend strongly on the assumed value of m^*, is much better and, in practice, 1% may be achieved.

Finally, one should say that similar experimental results were obtained in our laboratory for sputtered silver (Ag) and copper (Cu) films.

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