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Mean free path and density of conductance electrons in platinum determined by the size effect in extremely thin films

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A new method was developed to determine the mean free path, l_∞, and the conductivity, σ_∞, of charge carriers in metals by investigating the thickness dependence of the conductivity of thin films. The method includes also surface effects as given by the specularity parameter p and the surface roughness amplitude h. Experimental data taken during film growth could be fitted to theoretical size-effect relations only if nonzero specularity and heterogeneous film cross section caused by the surface roughness is introduced. The method allows determination of the Fermi-surface area and the electron density of the isotropic (amorphous) films. Both are smaller than expected from published bulk material data.

I. INTRODUCTION

The conductivity of a cubic metal in zero magnetic field is given by

$$\sigma_0=\frac{e^2}{12\pi^3}\int_{S_F}\vec{l}_k\cdot d\vec{S}_F=\frac{e^2}{12\pi^3\hbar}S_F l_0 \ , \qquad (1)$$

where $\vec{l}_k=\vec{v}_k\tau_k$ is the mean free path of an electron with velocity $\vec{v}_k$. The value of σ_0 is determined by the area of the Fermi surface, S_F, and the mean free path, l_0, of the electrons. It would be desirable to deduce the value of these two parameters separately rather than their product. Attempts have been made by introducing experimental conditions which influence the mean free path of the electrons in a measurable manner: (i) application of magnetic fields; (ii) high-frequency methods; and (iii) investigations of thin films with thicknesses comparable to the mean free path. The latter method is usually referred to as "size effects" in the literature. Studying the thickness dependence of the conductivity of thin films is expected to give information about the mean free path of the charge carriers. Fuchs[1] solved Boltzmann's equation, including boundary conditions at the film surface. His relation describes the thickness dependence of the conductivity

$$\sigma(d)=\sigma_\infty\left\{1-\frac{3}{2}\frac{l_\infty}{d}(1-p)\int_1^\infty\left\{(t^{-3}-t^{-5})\left[1-\exp\left(-\frac{d}{l_\infty}t\right)\right]\Big/\left[1-p\exp\left(-\frac{d}{l_\infty}t\right)\right]\right\}dt\right\} \ , \qquad (2)$$

where the thin metal film is bounded by two parallel planes with the separation d (film thickness) and where σ_∞ and l_∞ are conductivity and mean free path, respectively, of a film of infinite thickness. These values may differ from the related values σ_0 and l_0 for crystalline bulk material, because of the much larger density of defects and grain boundaries in thin polycrystalline fims. When deriving Eq. (2) Fuchs assumed a spherical Fermi surface for the conduction electrons. He further assumed that a fraction p of the electrons is specularly reflected at the surface while the remainder $1-p$ is diffusely scattered. Fuchs's assumptions are critically reviewed by Chambers.[2]

The size effect is caused by diffuse scattering of free charge carriers at the surface of thin films, therefore the specularity parameter is of fundamental interest. It is the subject of some controversy. Authors of theoretical papers tend to assume $p=0$, at least for metal surfaces, assuming totally diffuse scattering of the electrons at the surface. This opinion is supported by Soffer's[3] calculations on the influence of surface roughness and angle of incidence on scattering of electrons, after which diffuse scattering is expected as soon as the surface roughness exceeds the free-electron Fermi wavelength λ_F. For metals this wavelength is of the order of the atomic separation in solid samples. Because any metal surface should be expected to show this roughness, scattering of the electrons at the surface must be expected to be diffuse.

From the experimental point of view, interpretation of the results concerning the specularity is far from unique. Summaries of experimental data are given in review articles by Chopra,[4] Larson,[5] Coutts,[6] and Wissmann.[7] Almost all values of p between 0 and 1, and even unphysical values of $p < 0$ are used to explain the experimental results. In a great number of experiments the measured relation between resistivity and film thickness could be fitted to the theory only if values of $p \neq 0$ were assumed. But even with this assumption, a sufficient fit could be made only for films thicker than the mean free path or at least thicker than 100 Å. In other cases the curves could be fitted only in certain intervals of the film thickness. Thinner continuous films usually were excluded from the discussion. The general observation is that, in thinner films, even if they are continuous, the conductivity decreases much faster than expected from Fuchs's theory using a specularity parameter between 0 and 1. Boundary conditions in which the specularity parameter depends on the angle of incidence, θ, were introduced by Parrot[8] and Brändli and Cotti.[9] Below a critical angle, θ_1, the electrons were assumed to be diffusely scattered ($p=0$) and above this angle they are supposed to be specularly reflected ($p=1$). For $\theta_1 = 90°$ the thickness dependence is the same as in Fuchs's calculation for $p=0$. All theoretical curves for $\theta_1 < 90°$ show a slower increase of the resistivity with decreasing film thickness than in Fuchs's relation [Eq. (2)]. Experimentally, however, metal films always show a stronger increase. The angle of incidence hypothesis, therefore, seems to be unable to solve the transport problem of the very thin continuous films.

Grain boundary scattering was introduced by Mayadas and Schatzkes[10] as an extra effect. As shown by Tellier[11] this effect introduces an effective conductivity σ_∞ and mean free path l_∞ which differ from the single-crystal values σ_0 and l_0. It does not induce a thickness dependence as long as the crystallite size (film structure), D, and the reflection coefficient, R, of the electrons at the grain boundaries remain constant independent of the film thickness. To take the thickness dependence of the mean crystallite size, D, as well as of the unknown reflectance, R, into account introduces too many parameters. The homogeneous structure through the film thickness received special attention in a recent paper by Bergmann[12] where he reported evaporating the metal film under investigation onto metal-coated quartz substrates at 10 K.

In the present paper we report on investigations of the conductivity of very thin continuous platinum films (thickness $d \leq 3$ nm) for which special care was taken to keep the film structure independent of the film thickness. Platinum films have been also investigated by Heras[13,14] starting with thickness above 3 nm. It will be shown that the deviations between measured and calculated thickness dependence of the resistivity observed by others can be related to the heterogeneous cross section of the film, which defines the surface roughness. With this geometrical effect included, the observed transport data can be completely fitted leading to a specularity parameter p as well as σ_∞ and l_∞. The combination of this fit with the high sensitivity of the experiment gives hope that surface scattering can be investigated in detail.

II. THEORY

Fuchs introduced a quantitative theory of the thickness dependent conductivity by assuming that in the mean a fraction $1-p$ of the electrons is diffusely scattered at the surfaces during multiple scattering at both surfaces. In this theory the film is bounded by two parallel planes with separation d (film thickness). Two possible causes of diffuse scattering are: (i) local defects at the surface; and (ii) surface roughness as is usually observed in polycrystalline materials due to film nucleation and growth.

Ziman[15] calculated the specularity parameter due to surface roughness assuming that crystallites with a mean height h surmount the mean film thickness. Soffer[3] corrected Ziman's calculation by taking care of the flux-conservation requirement.

Surface roughness exhibits another effect on the measured conductivity which is not included in the specularity parameters. As mentioned first by Wedler[16] and then treated by Namba,[17] surface roughness leads to heterogeneous film cross section which must be considered when calculating a mean conductivity. A complete theory of the conductivity of realistic thin films exhibiting surface roughness must include effects both of the specularity parameter and of the film cross section.

The thickness of a realistic film is given in a one-dimensional approximation by

$$d(x) = \bar{d} + \Delta d(x) \ . \tag{3}$$

Using the same arguments as Fuchs the local conductivity $\sigma(x,d(x))$ is given by introducing Eq. (3) into Eq. (2),

$$\sigma(x,d(x)) = \sigma_\infty \left\{ 1 - \frac{3}{2} \frac{l_\infty}{d(x)} [1-p(x)] \right\} \int_1^\infty \left\{ (t^{-3} - t^{-5}) \left[1 - \exp\left(-\frac{d(x)}{l_\infty} t \right) \right] \bigg/ \left[1 - p(x) \exp\left(-\frac{d(x)}{l_\infty} t \right) \right] \right\} dt \ . \tag{4}$$

In the experiment, we measure the resistance, R, of the film and the mean film thickness $\bar{d}$ as well as the film length, L, and width b, respectively. From these data a mean conductivity can be calculated which is to be compared with the theory

$$R = \frac{1}{b}\int_0^L \frac{\rho(x,d(x))}{d(x)}dx = \frac{1}{b}\int_0^L \frac{dx}{\sigma(x,d(x))d(x)} .$$

The mean conductivity $\langle \sigma(\bar{d}) \rangle$ comparable to the experiment, then is defined by

$$\frac{\langle \sigma(\bar{d}) \rangle}{\sigma_\infty} = \frac{L}{\bar{d}}\left[\int_0^L \left(\frac{\sigma_\infty}{\sigma(x,d(x))d(x)}dx\right)\right]^{-1} . \qquad (5)$$

The denominator in Eq. (5) is given by Eq. (4). The integral of Eq. (5) cannot be traced analytically. For numerical calculations we approximated Δx of Eq. (3) by

$$\Delta x = h \sin\frac{2\pi x}{s} \qquad (6)$$

with the surface roughness amplitude, h, and the surface roughness wavelength s.

Beside the problems arising with the specularity parameter $p(x)$ mentioned above, one has to keep in mind that the topology of the surface at the film-vacuum interface is expected to differ from that of the film-substrate interface. This leads to different specularity parameters p and q at both of the surfaces, as treated by Lucas.[18] In the present paper we neglected the existence of two different specularity parameters for reasons explained in the discussions.

The purpose of the present paper is to deduce the transport parameters, σ_∞, l_∞, p, and the surface roughness amplitude, h, from the measured thickness dependent conductivity $\langle \sigma(\bar{d}) \rangle$ by computer fitting of the theoretical relation (5) to the measurements. The fitting makes sense only as long as during the film growth the mean free path l_∞ and the conductivity σ_∞ due to volume scattering and the surface roughness, h, remain constant, i.e., as long as the intrinsic structure and the surface topology of the films do not change during evaporation.

III. EXPERIMENTAL

The samples were prepared by electron gun evaporation in an oil free ultrahigh vacuum system. Before evaporation the pressure was about 10^{-9} mbar and during evaporation it was always less than 10^{-7} mbar. The substrates were glass slides (26×76 mm^2), which were carefully cleaned, coated with silver contacts, and annealed for about 4 h at 300 °C under vacuum conditions before evaporation. The sample geometry is shown in Fig. 1. The active film area for the conductivity measurements was 2×2 mm^2. The film thickness was monitored by a quartz oscillator with a sensitivity of 127 ± 10 Hz/nm for platinum. Special care was taken to calibrate the film thickness. The substrate temperature during evaporation was room temperature in most cases, and the evaporation rate was varied between 0.05 and 0.3 nm/sec.

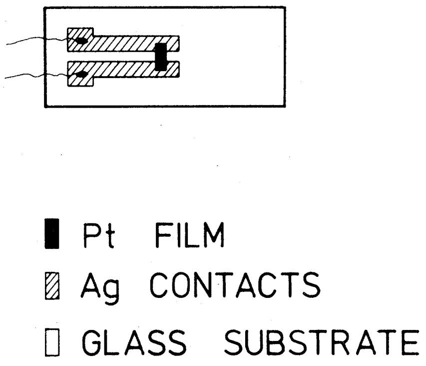

FIG. 1. Film geometry.

The thickness dependence of electric resistance was investigated *in situ* during evaporation. A constant voltage was applied to the silver contacts and the current through the sample was measured during evaporation as a function of the film thickness. (For an example of related plots see Figs. 4–6.) To improve the sensitivity of the experiment the metal vapor beam was mechanically chopped. The chopper was correlated to a lock-in amplifier allowing phase-sensitive measurements of the current as well as the derivative of the current by the film thickness versus film thickness.

A block diagram of the apparatus is given in Fig. 2. The metal is evaporated by an electron gun. The atomic beam is interrupted by a motor-driven chopper (chopping frequency 30 Hz). A condenser traps the ions as well as the electrons occurring together with the atom beam impinging at the film substrate. The ion current was taken for measurement and control of the evaporation rate which in this case was much more effective than using the signal of the quartz oscillator. A preamplifier was mounted inside of the vacuum vessel to increase the signal-to-noise ratio of the entire amplifying equipment. With the use of a sample and hold amplifier the current through the film was always registered when the chopper shut off the atom beam. In this way $I(t)$ (t = evaporation time) as well as $\Delta I/\Delta t$ could be measured. The quartz oscillator registered the thickness $d(t)$. From the ion current we obtained the evaporation rate $r = \Delta d/\Delta t$. All these signals were amplified by lock-in technique. From the combination of the signals the dependencies I vs d and dI/dd vs d were obtained and simultaneously plotted. A more detailed description of the equipment is given by Fischer *et al.*[19]

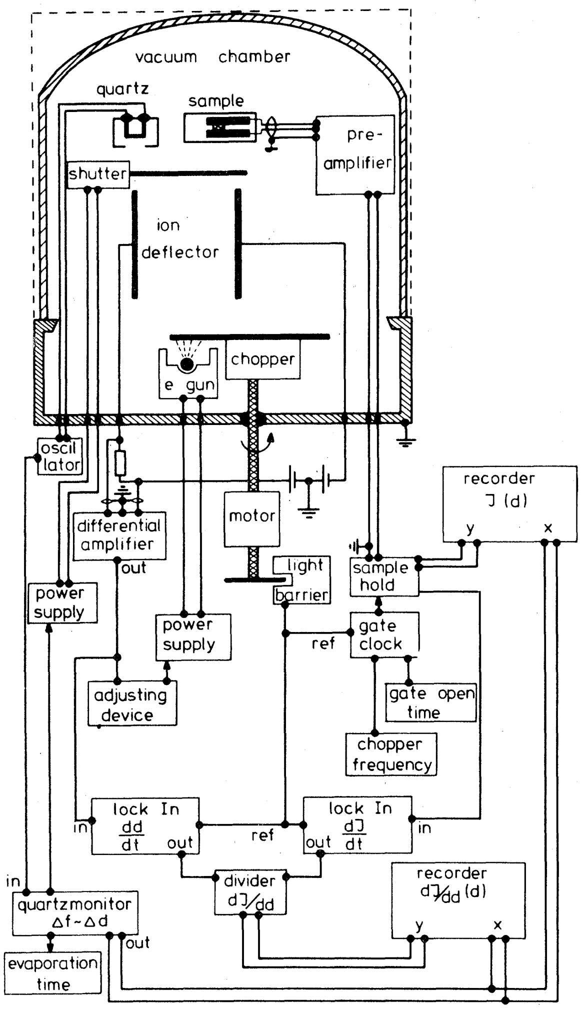

FIG. 2. The evaporation and registration equipment.

The sensitivity is such that the increase of the current related to an increase of the mean film thickness by $\frac{1}{400}$ of an atomic layer could be registered. The thickness of the evaporated films ranged from 0 to 3 nm. These films were about amorphous with a faint (111) texture perpendicular to the film plane, as observed for some of the films. This can be related to a cubic dense packing of the few atomic layers. Some of the films have been dissolved from the substrates and prepared for electron transmission and diffraction observations. Figure 3 gives a diffraction pattern of a 2 nm thick film. The halo, the photodensitometer traces, and the radial distribution function calculated from the traces count for an amorphous structure. Microcrystallites, if they exist, must be smaller than 1 nm in diameter. The transmission images (bright and dark field) with a point resolution of 0.8 nm showed a completely homogeneous film without any observable pinholes in it. So we conclude that these films are amorphous and continuous.

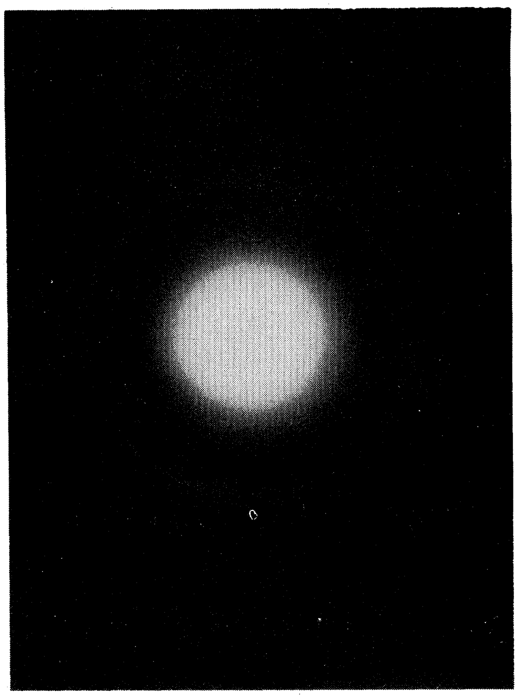

FIG. 3. Electron diffraction pattern of a 2 nm thick platinum film.

Since the diffraction pattern and transmission images remain the same for the thickest films under investigation we assume that the intrinsic structure of the investigated films is independent of the film thickness.

The films are continuous down to a thickness of a few monolayers. Figures 4 through 6 showed Ohmic conductivity inserted at mean thicknesses d_Ω between 0.6 nm [Figs. 4(a) and 4(b)] and 0.3 nm [Figs. 6(a) and 6(b)]. The onset of conductivity is very clearly shown in the dI/dd vs d curves. At thicknesses larger than d_Ω, island formation of the films can be excluded. The conductance dI/dU of these very thin films was purely Ohmic as shown, for example, in Fig. 7 for a 0.5 nm thick film where the conductance is independent of the applied voltage. The maximum voltage was related to a current density of 30 A mm^{-2}. Higher densities were not applied because of the related Ohmic heating. Island films would show much smaller conductance and would exhibit an increase of the conductance with increasing field. Finally the temperature dependence of the resistance showed for a 0.6 nm thick film the same behavior (Fig. 8) as known for much thicker evaporated continuous metal films. The resistance first decreased irreversibly with increasing temperature due to short-range-ordering effects of the atomic arrangements. Below the maximum annealing temperature reversible temperature dependence with positive temperature coefficient of resistivity is to be observed.

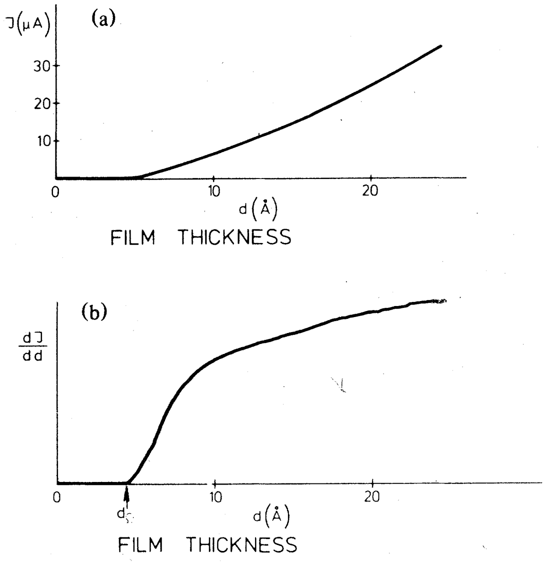

FIG. 4. (a) The current through the film vs film thickness. (b) The derivative of the current by the film thickness vs film thickness. Both curves were plotted during the evaporation. Evaporation rate $r = 0.10$ nm sec^{-1}.

IV. RESULTS

From the measured $I(d)$ curves as given by Figs. 4–6 and from the geometrical dimensions of the films the mean conductivity $\langle\sigma(\bar{d})\rangle$ was calculated. This can be eased by directly digitizing I and d during evaporation. The theoretical $\langle\sigma(\bar{d})\rangle$ behavior as given by Eq. (5) was computer fitted to the experimental curve by optimizing σ_∞, l_∞, h, and p as fitting parameters. The number of fitting parameters could be reduced by one if one introduces charge conservation in the free-electron model, which leads to

$$\frac{\sigma_\infty}{l_\infty}=\frac{\sigma_0}{l_0}=\left(\frac{8\pi}{3}\right)^{1/3}\frac{e^2}{h}n^{2/3} . \tag{7}$$

Conductivity and known or assumed mean free path in bulk undistorted material are σ_0 and l_0, respectively. The known or assumed density of free charge carriers is n. We avoided the use of bulk material values because of some uncertainties. Instead, we in-

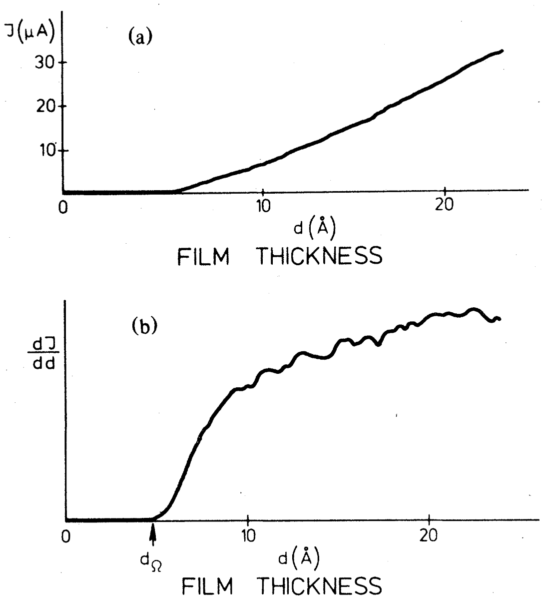

FIG. 5. (a) The current through the film vs film thickness. (b) The derivative of the current by the film thickness vs film thickness. Evaporation rate $r = 0.15$ nm sec^{-1}.

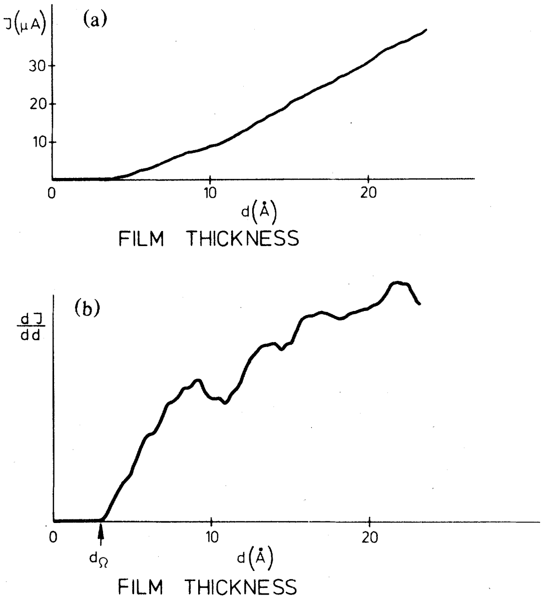

FIG. 6. (a) The current through the film vs film thickness. (b) The derivative of the current by the film thickness vs film thickness. Evaporation rate $r = 0.28$ nm sec^{-1}.

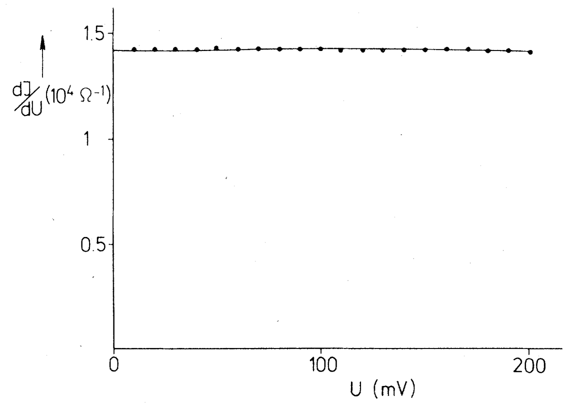

FIG. 7. Dependence of the conductance of a 0.5 nm thick film on the applied voltage.

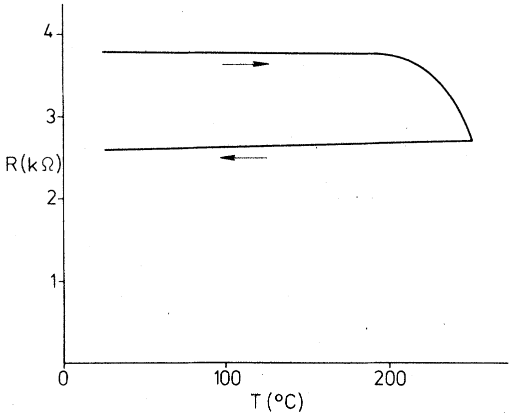

FIG. 8. Temperature dependence of the resistance of a 0.6 nm thick film.

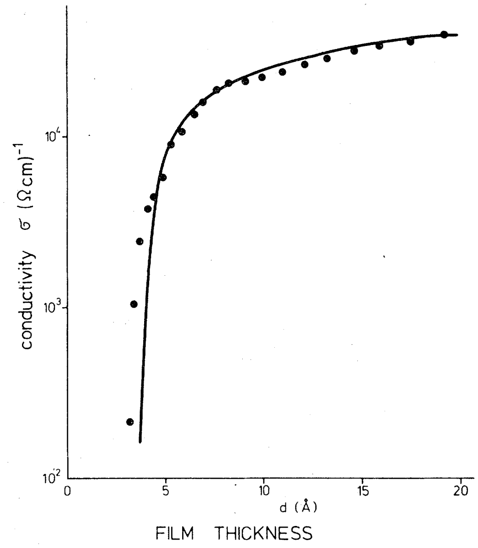

FIG. 9. The thickness dependence of the conductivity from measurements (dots) and from fit of Eq. (5) with parameters $\sigma_\infty = 5.96 \times 10^4$ $(\Omega\,\mathrm{cm})^{-1}$, $l_\infty = 11.7$ nm $p = 0.13$, and $h = 0.3$ nm.

tended to introduce the thin film investigations as an independent and additional method of determining the transport parameters.

The amount of the surface roughness amplitude, h, must be close to the critical mean thickness, d_Ω, at which Ohmic conductivity occurs and which clearly can be determined from the experimentally observed dI/dd curve [Figs. 4(b), 5(b), and 6(b)]. The restriction $h \gtrsim d_\Omega$ decreases the uncertainty about the amount of the fitting parameter drastically. A more detailed justification of this treatment will be given in an upcoming paper[20] where gold films with surface roughness amplitudes $h \approx 10$ nm were investigated.

Figure 9 gives an example of the fit (film of Fig. 6). The dots are the experimental $\langle \sigma(\bar{d}) \rangle$ values; the curve gives the fit with the parameter mentioned in the caption. The small deviations at thicknesses larger than 0.5 nm are due to the quantum size effect.[21,22] The deviations at thicknesses below 0.5 nm are due to the approximations of theory. At $d \leq 0.5$ nm more than 50% of the film cross section is surface roughness. In this case the theory introduced above contains too crude approximations.

Table I gives the computer-fitted data for films evaporated at 300 K. The films differ solely in the evaporation rate. The method allows separation of σ_∞ and l_∞ and therefore determination of the ratio l_∞/σ_∞, which according to Eq. (7) leads to the density of the free charge carriers.

The surface roughness depends on the evaporation rate as shown in Fig. 10. Higher evaporation rates produce smaller surface roughness.

V. DISCUSSION

Platinum films evaporated with a rate of 0.3 nm sec^{-1} onto glass substrates are smooth at the surface in atomic dimensions. The surface roughness increases with decreasing evaporation rate. The thickness dependence of the conductivity of these very thin films ($d << l_\infty$) needs to be treated with the complete Fuchs's equation including the surface roughness [Eq. (5)] instead of Sondheimer's approxi-

TABLE I. Transport and surface parameters σ_∞, l_∞, p, and h evaluated from computer fitting of experimental $\langle \sigma(\bar{d}) \rangle$ curves. The platinum films were evaporated at room temperature.

Film	Evaporation rate (nm^{-1})	σ_∞ [$10^4(\Omega\,\mathrm{cm})^{-1}$]	l_∞ (nm)	p	h (nm)	l_∞/σ_∞ [$10^{-12}(\Omega\,\mathrm{cm}^2)$]
1	0.10	6.20	13.0	0.13	0.51	20.97
2	0.15	6.32	12.8	0.15	0.55	20.25
3	0.28	5.96	11.7	0.13	0.31	20.56
4	0.30	5.60	10.5	0.14	0.31	18.75

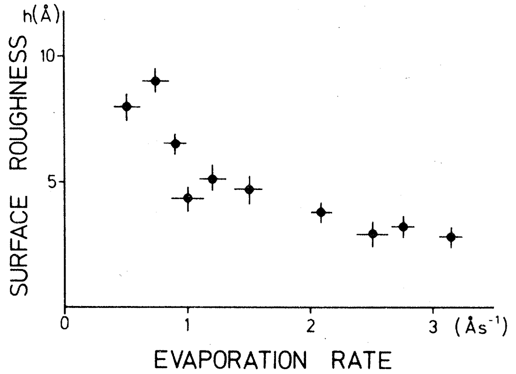

FIG. 10. The surface roughness amplitude, h, as determined from curve fitting vs evaporation rate for films evaporated at room temperature.

mation[23]

$$\frac{\sigma}{\sigma_\infty}=\left[1+\frac{3}{8}\frac{l_\infty}{d}(1-p)\right]^{-1}, \tag{8}$$

which is usually referred to in the literature. Conductivity measurements and computer fits of films with thicknesses small compared to the mean free path allow the separation of l_∞ and $(1-p)$ which is impossible by applying Sondheimer's relation.

We believe that the introduction of the surface roughness causing heterogeneous film cross section allows a good explanation of the data. Figure 11 gives an example of the fitting. The dots are again the experimental results for $\langle\sigma(d)\rangle$. Curve 2 is the best fit assuming totally diffuse scattering ($p=0$) of the charge carrier at the surface and neglecting surface roughness ($h=0$). Fuchs's equation (2) was used for the fitting with parameters $\sigma_\infty=17.2\times10^4$ $(\Omega\,\mathrm{cm})^{-1}$ and $l_\infty=18.6$ nm. Curve 1 includes nonzero specularity with parameters $p=0.24$, $\sigma_\infty=13.8\times10^4$ $(\Omega\,\mathrm{cm})^{-1}$, and $l_\infty=20.4$ nm. Neither curve follows the steep decrease of conductivity at decreasing film thickness below 0.8 nm. In both cases the conductivity σ_∞ is larger than the known value for bulk materials which makes no sense. In the third curve a surface roughness was introduced. The curve obtained from Eq. (5) with parameters $\sigma_\infty=8.85\times10^4$ $(\Omega\,\mathrm{cm})^{-1}$, $l_\infty=7.4$ nm, $p=0.16$, and $h=0.3$ nm fits the experimental results down to a mean film thickness of about 0.4 nm. Again the small deviations of the experimental data from the fitting curve 3 are caused by the quantum size effect.

We also tried to fit the experimental data with $h\neq0$ and $p=0$, but did not succeed. This means one has to admit a certain amount of specularity ($p\neq0$). This point will be stressed in another paper.[20] In addition, the existence of the quantum size effect[21,22] demands $p\neq0$.

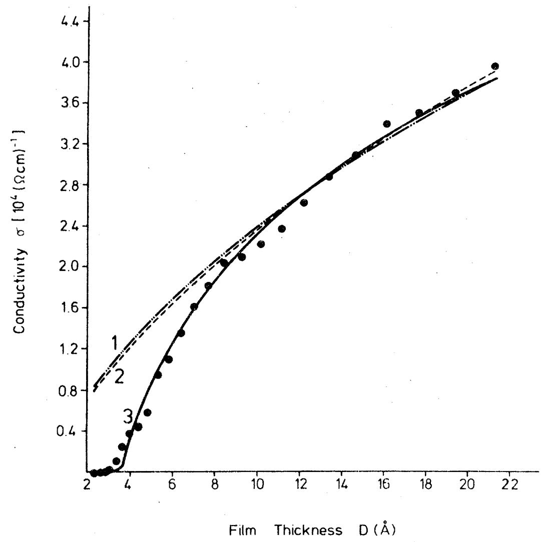

FIG. 11. The dependence of the conductivity on the film thickness experimental data: dots 1: fitted with Fuchs's theory, assuming $p=0.24$, $\sigma_\infty=13.8\times10^{-6}$ $(\Omega\,\mathrm{cm})^{-1}$, and $l_\infty=20.4$ nm; 2: fitted with Fuchs's theory assuming $p=0$, $\sigma_\infty=17.2\times10^{-4}$ $(\Omega\,\mathrm{cm})^{-1}$, and $l_\infty=18.6$ nm; and 3: fitted with the modified Fuchs's theory including surface roughness assuming parameters $p=0.16$, $\sigma_\infty=8.85\times10^{-4}$ $(\Omega\,\mathrm{cm})^{-1}$, $l_\infty=7.4$ nm, and $h=0.3$ nm.

The computer fit as given by Fig. 11 states that the conductivity in very thin film is very sensitive to surface effects. Just these effects can be used to determine the wanted bulk material data.

The results of the investigation of films evaporated at room temeperature are given in Table I. The conductivity, σ_∞, as well as the mean free path, l_∞, decrease at an increasing evaporation rate. This is caused by an increase of contaminations due to an increase of the vacuum pressure as well as by higher disorder in the atomic arrangement. The conductivity is in all cases smaller than the bulk value, $\sigma_0=9.35\times10^4$ $(\Omega\,\mathrm{cm})^{-1}$. The lower values are expected, due to the quasiamorphous structure of the films. The mean free path l_∞ at room temperature is about 10 nm. The often-used argument that the mean free path in amorphous material is of the order of atomic distances does not hold for the quasiamorphous platinum films.

The specularity parameter, p, seems to be independent of the surface roughness, but the number of samples is too small to draw any conclusion. In Sec. II we introduced a mean value at the surface which included also scattering from surface elements with normals parallel to the current. Further, we assumed the same specularity parameter for both surfaces, which contradicts the reality. The curve fitting which we used could be done also for two specularity parameters, p and q, introduced by Lucas.[18] Since fitting to one more parameter would result in a larger uncertainty of the results, we avoided it. Juretschke[24] showed that the determination of only one specularity parameter expresses an average value of both.

The surface roughness amplitude, h, is extremely small. These values are unique for platinum films evaporated at room temperature. No other metal investigated so far (gold, aluminum, palladium, nickel, copper, or silver) led to films as smooth as platinum. The amount of the surface roughness obtained from the curve fitting was always about the same as the mean minimum thickness, d_Ω, for Ohmic conductivity. As shown in Fig. 10, h decreases with increasing evaporation rate. Surface roughness therefore is due to nucleation of atomic clusters at the substrate. The smaller the nuclei are, the smaller is the surface roughness.

Of special interest is the Fermi surface in the metal films. Due to the quasiamorphous structure it is supposed to be spherical

$$S_F = \frac{6\pi^2}{e^2}\frac{\sigma_\infty}{l_\infty} \quad . \tag{9}$$

From Table I follows the average value of $(l_\infty/\sigma_\infty) = 20.13 \times 10^{-16}$ (Ω m^2) which leads to $S_F = 7.61 \times 10^{20}$ m^{-2}. Further the electron density

$$n_\infty = \left(\frac{3}{8\pi}\right)^{1/2}\left(\frac{h}{e^2}\right)^{3/2}\left(\frac{\sigma_\infty}{l_\infty}\right)^{3/2} \tag{10}$$

amounts to $n_\infty = 1.6 \times 10^{28}$ m^{-3} if all the conductivity results from the $6s$ electrons. This would lead to 0.24 free electrons per platinum atom, a value which should be compared with that of bulk material. Band calculations by Anderson[25] and experiments by Windmiller[26] showed that platinum is a two-band conductor (s-like electrons in closed and d-like holes in open Fermi surfaces). According to Anderson, the number of free electrons and holes should each be 0.405 per atom which each is about twice as large as we find in our experiments.

From the two-band model ($\sigma_0 = \sigma_e + \sigma_h$), Dosdale and Livesey[27] calculated for bulk material

$$\frac{\sigma_h}{\sigma_e} = 0.87 \quad ,$$

which leads to $\sigma_e = 5.13 \times 10^6$ (Ω cm)$^{-1}$, a value which is close to the one we found for σ_∞. Here the question arises "what happened then to the contribution of the holes if the conductivity of extremely thin films is only due to electrons?"

Analyzing our data on the known fact that platinum is a two-band conductor

$$\sigma = \sigma_e + \sigma_h, \quad \sigma_\infty = \sigma_{e\infty} + \sigma_{h\infty} \quad ,$$

with $\sigma_e/\sigma_{e\infty}$ and $\sigma_h/\sigma_{h\infty}$ obeying the relations used above would force us to introduce different specularity parameters, p_e and p_h for electrons and holes. The mean effective mass for electrons $m_e^* = 2.76 m_0$ and holes $m_h^* = 4.34 m_0$ leads to a smaller Fermi wavelength for the holes than for the electrons. By this, one should assume $p_h < p_e$ if scattering at the surface depends on the Fermi wavelength of the free charge carriers. This would remarkably decrease the contribution of the holes to the conductivity of the very thin films. Furthermore, it is questionable that the ratio σ_h/σ_e, calculated by Dosdale and Livesey[27] is valid for our films with an extremely distorted structure. One might assume that holes are scattered much more by the distortions than electrons because of their larger effective mass ($\sigma_{h\infty} << \sigma_{e\infty}$) which would approximate a one-band rather than a two-band conductor.

VI. CONCLUSION

Size effects on the conductivity increase drastically when the film thickness is small compared to the mean free path of the charge carriers. Investigations in this thickness region are very promising for the determination of fundamental electronic transport properties. The combination of high sensitive conductivity measurements and computer fitting of Fuchs's modified theory allows the determination of σ_∞, l_∞, p, and h. The theory must include the heterogeneous film cross section. Partly specular reflection of the electrons at the surface has to be admitted to explain the experimental results. The experiment is sensitive enough to reveal the influence of additional scattering centers at the surface, which can be added in a controllable manner.

The electron density and Fermi surface of platinum films are smaller than expected from assumed bulk material values. The same observation is valid for a number of other metals investigated in the literature. In addition, platinum raises questions because of its two-band conductivity. Galvanomagnetic investigations of thin films are needed to deal with these problems. Furthermore, information is expected from the observation of the temperature dependency of the above-discussed effects.

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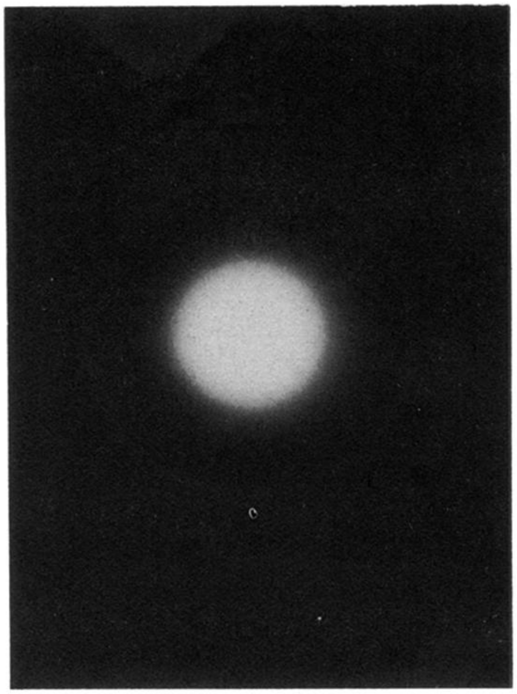

FIG. 3. Electron diffraction pattern of a 2 nm thick platinum film.