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Optical properties of free-electron metal films including electron surface scattering: Theory

F. E. Hutchison and W. N. Hansen
Utah State University, Logan, Utah 84322

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The present understanding of the optical and electrical properties of free-electron metal (FEM) films does not permit the optical characteristics to be related to the dc conductivity in terms of the microscopic parameters when both the optical and electrical characteristics are being measured simultaneously. To resolve this dilemma, a new set of expressions for the reflectance and transmittance of thin FEM films is developed from the work of Reuter and Sondheimer. The expressions are used to calculate the effects of electron scattering from the internal surface of a hypothetical gold film. The results demonstrate that it should be possible to determine the microscopic parameters of a thin film from optical measurements.

I. INTRODUCTION

Recent work with halide adsorption on gold films[1-3] has raised serious doubts about the present understanding of the optical and electrical properties of thin films because no current theory can explain the effects observed. The dilemma is that changes in the optical characteristics of gold films induced by I^- adsorption cannot be related to changes in the dc conductivity in terms of the microscopic parameters when both the optical and electrical characteristics are being measured simultaneously. A single physical description of a thin film which could account for optical and electrical properties is needed. In the case of free-electron metals (FEM, i.e., simple metals, such as sodium, and Au, Ag, and Cu) much work has been done by describing the FEM in terms of electron density, N, mean free path, l, fraction of electrons scattered specularly at the surfaces, p, and a number to account for interband transitions and core electrons, S.

In this paper, the theory of the optical properties of FEM with surface scattering of electrons is developed for films from Maxwell's equations and Boltzmann transport theory. The resulting expressions describe reflectance and transmittance of films in terms of their microscopic parameters. The expected optical response of gold films is calculated using reported microscopic parameters of bulk gold and the effects of surface scattering of electrons.

Reuter and Sondheimer[4] were the first to consider what effect surface scattering of electrons had on the optical properties of FEM. Their work was concerned with reflection from semi-infinite FEM at whose surface a fraction, p, of the electrons were scattered specularly; the rest, $1-p$, were diffusely scattered. Holstein[5] used energy considerations to evaluate the absorptivity of light incident normal to a FEM surface as a function of p. Dingle[6] showed that Holstein's results were the same as Reuter and Sondheimer's and expressed the theory in dimensionless form. He applied the theory to bulk FEM under varying circumstances[6-8] and to films of arbitrary thickness with totally diffuse scattering.[9] Most workers since Dingle have considered either totally specular or totally diffuse scattering on bulk FEM,[10-19] with some films[20-25] being considered. There have been corrections introduced to account for oblique incidence in the cases of p-polarized (TM) and s-polarized (TE) light. Also, new mathematical techniques have been used to obtain more precise results than Dingle. This paper presents a more detailed set of expressions for the reflectance and transmittance of FEM films than has been reported previously.

II. THEORY

The arguments used by Reuter and Sondheimer[4] for deriving the integro-differential equation obeyed by the electric field in a bulk FEM can be extended to films with very little difficulty (see Appendix). The resultant equation is

$$\frac{d^2E(z)}{dz^2}+\frac{\omega^2l^2S}{c^2}E(z)=\iota\alpha\left[p\int_{-d}^{0}E(y)\int_1^\infty e^{-sw|z-y|}\left(\frac{1}{s}-\frac{1}{s^3}\right)ds\,dy+\int_0^dE(y)\int_1^\infty e^{-sw|z-y|}\left(\frac{1}{s}-\frac{1}{s^3}\right)ds\,dy\right], \qquad (1)$$

where z is the depth into the film, d is the thickness of the film, l is the mean free path in the bulk material, $w = 1 + \iota\omega\tau$ with $\omega = 2\pi f$, f being frequency and τ being the electronic relaxation time, $\alpha = 8\pi^2\omega e^2 m^2 v^2 l^3/c^2 h^3$ with m being the effective electronic mass, v is the Fermi velocity, c is the velocity of light, and h is Planck's constant. All distances are in terms of l and ι is $\sqrt{-1}$.

The above equation for the electric field may be solved in closed form only for $p = 0$ and $p = 1$. Since values of p between zero and one are desired, the above equation is solved by a series such as Dingle[9] found for the above equation when $p = 0$. Consider the possible solution

$$E_1(z) = e^{-uwz}\,, \tag{2}$$

which when substituted in Eq. (1) results in

$$w^2(u^2 + \eta S)e^{-uwz} = \left(\frac{\iota\alpha}{w}\right)\left[K(u)e^{-uwz} - e^{-uwd}\int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\frac{e^{sw(z-d)}}{s+u}\,ds \right.$$
$$\left. - pe^{-uwd}\int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\frac{e^{-sw(z+d)}}{s+u}\,ds - (1-p)\int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\frac{e^{-swz}}{s-u}\,ds\right], \tag{3}$$

where $\eta = (\omega l/cw)^2$ and

$$K(u) = \int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\left(\frac{1}{s+u} + \frac{1}{s-u}\right)ds = \frac{1}{u^3}\left[2u + (u^2-1)\ln\left(\frac{1+u}{1-u}\right)\right]. \tag{4}$$

If $u^2 = \xi K(u) + \eta$, where $\xi = \iota\alpha/w^3$, we cannot account for the three integrals on the right-hand side of Eq. (3). So, consider

$$E_2(z) = -\xi\left[e^{-uwd}\int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\frac{e^{-sw(d-z)}}{(s-u)(s^2-\eta)} + pe^{-uwd}\int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\frac{e^{-sw(z+d)}}{(s+u)(s^2-\eta)}\,ds \right.$$
$$\left. + (1-p)\int_1^\infty \left(\frac{1}{s} - \frac{1}{s^3}\right)\frac{e^{-swz}}{(s+u)(s^2-\eta)}\,ds\right]. \tag{5}$$

This leaves only terms of order ξ^2 so the process can be repeated to form a series in ξ. The solution is of the form

$$E_{\rm I}(z) = E_1(z) + E_2(z) + O(\xi^2)\,. \tag{6}$$

There is another solution, $E_{\rm II}(z)$, which is found by using $-u$ instead of u. The electric field is a linear combination of these two solutions

$$E(z) = AE_{\rm I}(z) + BE_{\rm II}(z)\,. \tag{7}$$

By using boundary conditions, we can obtain four relations between A, B, i, r, and t, where the latter are the incident, reflected, and transmitted amplitudes of the electric field. Consider that for perpendicular polarization the boundary condition is that the tangential components of the magnetic field must be equal across the boundaries,

$$H_1(0)_{\rm tang} = H_2(0)_{\rm tang}\,, \tag{8a}$$

$$H_2(d)_{\rm tang} = H_3(d)_{\rm tang} \tag{8b}$$

and from Maxwell's equations, the magnetic field is related to the curl of the electric field. For parallel polarization the same argument holds for the electric field instead of the magnetic field. However, for oblique incidence, the above expressions for the electric field must be re-derived for each polarization because the wave equation becomes a pair of coupled equations between the x and y components of the electric and magnetic fields. If, instead, the electric field (or the magnetic field, depending on the polarization) for normal incidence is multiplied by the cosine of the angle of incidence, and used as the tangential component, the result is a simple but good approximation. For the zeroth order in ξ (no surface considerations of electron scattering), this approximation gives the same results as the derivation of reflectance and transmittance using traditional optical constants.

For perpendicular (transverse electric or TE) polarization the four relations are

$$i + r = E(0)\,, \tag{9a}$$

$$t = E(d)\,, \tag{9b}$$

$$(i - r)n_1\cos\theta_1 = \frac{\iota}{\eta^{1/2}}E'(0)\cos\theta_2\,, \tag{9c}$$

$$tn_3\cos\theta_3 = \frac{\iota}{\eta^{1/2}}E'(d)\cos\theta_2\,. \tag{9d}$$

For parallel (transverse magnetic or TM) polarization they are

$$(i+r)\cos\theta_1 = E(0)\cos\theta_2 , \tag{10a}$$

$$t\cos\theta_3 = E(d)\cos\theta_2 , \tag{10b}$$

$$(i-r)n_1 = \frac{\iota}{\eta^{1/2}}E'(0) , \tag{10c}$$

$$tn_3 = \frac{\iota}{\eta^{1/2}}E'(d) . \tag{10d}$$

$E'(z)$ denotes differentiation of $E(z)$ with respect to z. Also, θ_m is the angle of incidence for phase m, and n_1 and n_3 are the optical constants of the first and third phase.

Approximations can be made which make calculations simpler and physical interpretations easier. For the electric field

$$E(z) = Ae^{-uwz} + Be^{uwz} \tag{11}$$

is a very good approximation because $|\xi| << 1$. Also, we can approximate $E'(z)$ by the expression

$$\begin{aligned} E'(z) = A\,\{&-uwe^{-uwz} - \xi w[e^{-uwd}\mathrm{Ei}(w(d-z)) - pe^{-uwd}\mathrm{Ei}(w(z+d)) - (1-p)\mathrm{Ei}(wz)]\} \\ &+ B\,\{uwe^{uwz} - \xi w[e^{uwd}\mathrm{Ei}(w(d-z)) - pe^{uwd}\mathrm{Ei}(w(z+d)) - (1-P)\mathrm{Ei}(wz)]\} , \end{aligned} \tag{12}$$

where

$$\mathrm{Ei}(wx) = \int_1^\infty \left(\frac{1}{s^2} - \frac{1}{s^4}\right) e^{-swx}\,ds , \tag{13}$$

because $|\eta| << 1$. For convenience, let

$$\frac{\iota}{\eta^{1/2}}E'(z) = Ae^{-uwz}n(z) - Be^{uwz}n'(z) . \tag{14}$$

Then

$$\begin{aligned} n(z) = -\frac{\iota w}{\eta^{1/2}}\{u - \xi e^{uwz}[&e^{uwd}\mathrm{Ei}(w(d-z)) \\ &- pe^{-uwd}\mathrm{Ei}(w(z+d)) - (1-p)\mathrm{Ei}(wz)]\} \end{aligned} \tag{15a}$$

and

$$\begin{aligned} n'(z) = -\frac{\iota w}{\eta^{1/2}}\{u - \xi e^{-uwz}[&e^{uwd}\mathrm{Ei}(w(d-z)) \\ &- pe^{uwd}\mathrm{Ei}(w(z+d)) - (1-p)\mathrm{Ei}(wz)]\} . \end{aligned} \tag{15b}$$

The quantity

$$\frac{-\iota wu}{\eta^{1/2}} = \left(1 - \frac{\iota\omega_p^2\tau}{\omega w} + S\right)^{1/2} , \tag{16}$$

where

$$\omega_p^2 = \frac{4\pi Ne^2}{m} , \tag{17}$$

is the familiar expression for the dielectric constant of a free-electron gas with corrections for interband transitions and the effect of core electrons. Therefore, $n(z)$ and $n'(z)$ act as optical constants containing both a bulk and a surface contribution.

Since the algebraic solutions of Eqs. (8) and (9) for the reflectance and transmittance are very involved, intermediate variables have been created to simplify the resultant expressions. For convenience, let

$$\xi_1 = n_1\cos\theta_1 , \tag{18a}$$

$$\xi_3 = n_3\cos\theta_3 = (n_3^2 - n_1^2\sin^2\theta_1)^{1/2} \tag{18b}$$

and

$$\xi(0) = n(0)\cos\theta_2 = \{[n(0)]^2 - n_1^2\sin^2\theta_1\}^{1/2} . \tag{18c}$$

The definitions of $\xi'(0)$, $\xi(d)$, and $\xi'(d)$ are analogous to that of $\xi(0)$ and

$$\alpha^+ = \frac{\xi_1 + \xi'(0)}{\xi_1 + \xi(0)} , \tag{19a}$$

$$\alpha^- = \frac{\xi_1/n_1^2 + \xi(0)/n(0)^2}{\xi_1/n_1^2 + \xi'(0)/n'(0)^2} \tag{19b}$$

and

$$\beta = \iota\eta[(-\iota uw/\eta)^2 - n_1^2\sin^2\theta_1]^{1/2}d . \tag{19c}$$

The quantities

$$r_{\perp 12} = \frac{\xi_1 - \xi(0)}{\xi_1 + \xi(0)} , \tag{20a}$$

$$r'_{\perp 12} = \frac{\xi_1 - \xi'(0)}{\xi_1 + \xi'(0)} , \tag{20b}$$

$$r_{\perp 23} = \frac{\xi(d) - \xi_3}{\xi(d) + \xi_3} , \tag{20c}$$

$$t_{\perp 12} = \frac{1 + \alpha^+ r_{\perp 23}e^{2\iota\beta} + r_{\perp 12} + r_{\perp 12}{}' r_{\perp 23}e^{2\iota\beta}}{1 + r_{\perp 23}e^{2\iota\beta}} , \tag{20d}$$

$$t_{\perp 23} = 1 + r_{\perp 23} , \tag{20e}$$

$$r_{\parallel 12} = \frac{n(0)}{n'(0)}\,\frac{\xi_1/n_1^2 - \xi(0)/n(0)^2}{\xi_1/n_1^2 + \xi'(0)/n'(0)^2} , \tag{20f}$$

$$r'_{\parallel 12} = \frac{\xi_1/n_1^2 - \xi'(0)/n'(0)^2}{\xi_1/n_1^2 + \xi'(0)/n'(0)^2} , \tag{20g}$$

$$r_{\parallel 23} = \frac{n(d)}{n'(d)}\,\frac{\xi(d)/n(d)^2 - \xi_3/n_3^2}{\xi'(d)/n'(d)^2 + \xi_3/n_3^2} , \tag{20h}$$

$$\begin{aligned} t_{\parallel 12} = &\frac{\alpha^- n(0) + n'(0)r_{\parallel 23}e^{2\iota\beta}}{n(0) + n'(0)r_{\parallel 23}e^{2\iota\beta}} \\ &+ \frac{r_{\parallel 12}n(0) + n'(0)r'_{\parallel 12}r_{\parallel 23}e^{2\iota\beta}}{n(0) + n'(0)r_{\parallel 23}e^{2\iota\beta}} \end{aligned} \tag{20i}$$

and

$$t_{\parallel 23} = 1 + \frac{n'(d)r_{\parallel 23}}{n(d)} , \tag{20j}$$

function as Fresnel reflection and transmission coefficients. Then, setting the incident amplitude to unity, the reflection and transmission coefficients become

$$r_\perp = \frac{r_{\perp 12} + \alpha^+ r_{\perp 23} e^{2\iota\beta}}{1 + r_{\perp 12}' r_{\perp 23} e^{2\iota\beta}} , \tag{21a}$$

$$r_\parallel = -\frac{r_{\parallel 12} + r_{\parallel 23} e^{2\iota\beta}}{\alpha^- + r_{\parallel 12}' r_{\parallel 23} e^{2\iota\beta}} , \tag{21b}$$

$$t_\perp = \frac{t_{\perp 12} t_{\perp 23} e^{\iota\beta}}{1 + r_{\perp 12}' r_{\perp 23} e^{2\iota\beta}} , \tag{21c}$$

$$t_\parallel = \frac{n(d)}{n'(0)} \frac{t_{\parallel 12} t_{\parallel 23} e^{\iota\beta}}{\alpha^- + r_{\parallel 12}' r_{\parallel 23} e^{2\iota\beta}} . \tag{21d}$$

The reflectance and transmittance are given by

$$R_\perp = |r_\perp|^2 , \tag{22a}$$

$$T_\perp = \frac{\mathrm{Re}\,\xi_3 |t_\perp|^2}{\xi_1} , \tag{22b}$$

$$R_\parallel = |r_\parallel|^2 , \tag{22c}$$

$$T_\parallel = \mathrm{Re}\left(\frac{n_1 \xi_3}{n_3 \xi_1}\right) |t_\parallel|^2 . \tag{22d}$$

These forms for $R_\perp$, $T_\perp$, $R_\parallel$, and $T_\parallel$ compare well with the traditional expressions for films. If the surface contributions are ignored (zeroth order in ξ), the above expressions reduce to those for reflectance and transmittance given by Hansen.[26]

III. RESULTS

Two interesting questions arise in connection with this work. First, can the above theory adequately describe the optical properties of thin films? And second, what are the effects of surface scattering on the optical properties of thin films?

In a later paper,[27] a procedure used to numerically invert the optical equations and determine the microscopic parameters of a gold film from optical measurements will be described. The results from a representative film were

$$N = 5.43 \times 10^{22}\ \text{electrons/cm}^3 ,$$

$$l = 45.8\ \text{Å},\quad S = 7.9,\quad p = 0.018$$

(determined from five transmission measurements at normal incidence at wavelengths between 16 000 and 20 000 Å, film thickness of 178.8 Å). The comparison between the experimental optical measurements and those predicted from the above parameters is shown in Fig. 1. The comparison is very good with most differences being less than 5%, even at wavelengths well removed from those used for the characterization. Much of the difference at shorter wavelengths can be attributed to the value of S changing as the photon energies approach the interband transition threshold. This demonstrates that the expressions contained herein can describe the optical properties of thin FEM films.

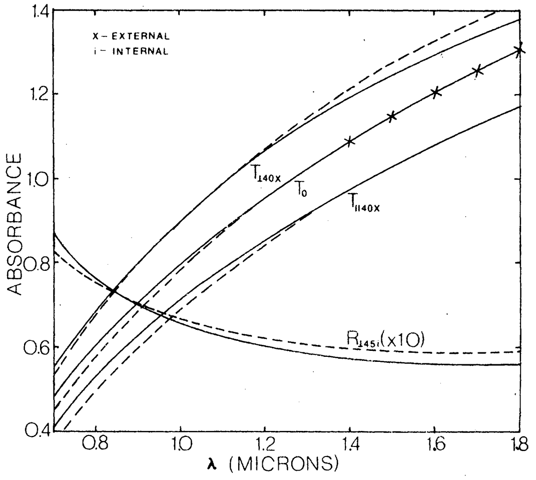

FIG. 1. Comparison of actual values of absorbance (–––) vs wavelength with predicted values (——) based on microscopic parameters determined from five transmission measurements (marked with ×'s). Parameters of film were $d = 178.8$ Å, $N = 5.43\times10^{22}$ electrons/cm^3, $l = 45.8$ Å, $S = 7.9$, $p = 0.018$, $n_1 = 1.00$, $n_3 = 1.50$, and $k_3 = 0.00$.

To see the effects of electron surface scattering reflectance and transmittance were calculated for a hypothetical film with the microscopic properties of bulk gold. The number of electrons/cm^3, N, was 5.9×10^{22}, and the mean free path l was 350 Å. The parameter S, which accounts for the effects of interband transitions and core electrons, was reported as a function of wavelength by Theye.[28] However, for convenience, an arbitrary value of 3.5 was used for S in all calculations. Other parameters of the film were

$$d = 100\ \text{Å},\quad n_1 = 1.50 ,$$

$$n_3 = 1.00,\quad k_3 = 0.00 .$$

Surface scattering has a second-order effect on the optical properties of FEM, as expected. This is clearly seen in a graph of internal reflectance as a function of angle of incidence (Fig. 2). Indeed, changes in p affect internal reflection (and internal ellipsometry, which is associated with internal reflection) more dramatically than changes in any other optical measurement. This is due to increased electric fields at the film surface for internal reflection.

The electrons are affected by surface scattering only when they interact with the surface. The smaller d/l, the more often the electrons interact with the surface. This can be shown by the difference in absorbance ($A = -\log_{10} R$) when p is changed from

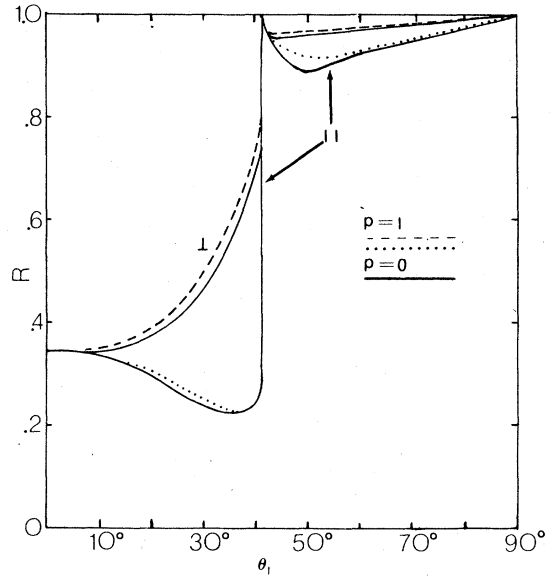

FIG. 2. Internal reflectance vs angle of incidence for parallel and perpendicular polarization showing the difference in reflectance caused by changing p from zero to one. Optical constants of bounding phases were $n_1=1.50$, $n_3=1.00$, and $k_3=0.00$.

zero to one for various values of l (Fig. 3). The increase in the difference as d/l becomes smaller confirms the dependency.

As the frequency of the electromagnetic radiation decreases. the electrons travel farther during the longer period of an individual photon vibration. Therefore, the difference in absorbance for a change from $p=0$ to $p=1$ is greater for the longer wavelengths because the electrons are more likely to interact with the surface. This clearly happens, as is shown in Fig. 4.

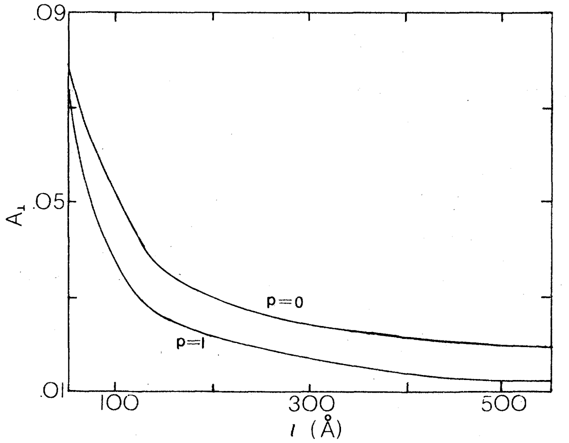

FIG. 3. Internal reflectance at 45 ° for a wavelength of 11 000 Å demonstrates the difference in absorbance ($A=-\log_{10}R$) as a function of mean free path for values of p equal to zero and one for a hypothetical film with the microscopic parameters of pure gold ($N=5.9\times10^{22}$ electrons/cm^3, $l=350$ Å, $S=3.5$) and a thickness of 100 Å.

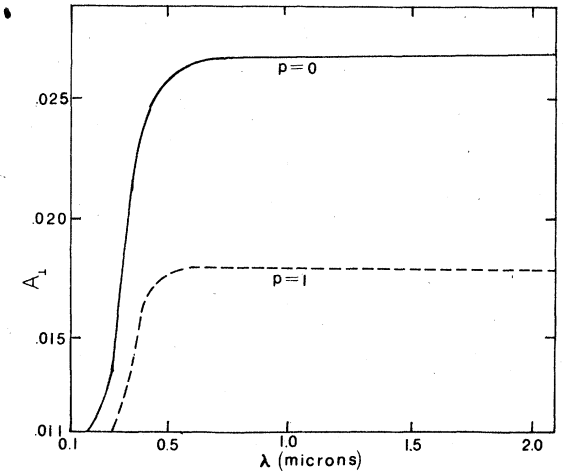

FIG. 4. Absorbance as a function of wavelength and surface scattering parameter, p, for internal reflectance at the critical angle of a hypothetical film with the microscopic parameters of pure gold and thickness 100 Å. This graph demonstrates the large change in absorbance for a change in p at long wavelengths, suggesting that optical measurements at such wavelengths could be used to determine the surface scattering parameter, p.

IV. SUMMARY AND CONCLUSIONS

Expressions have been developed for the reflectance and transmittance for FEM films. These expressions can describe the optical properties of thin FEM films, including the electron surface scattering, without the restrictions imposed by earlier papers. Furthermore, when the same assumptions are applied to these equations, the results of earlier papers are achieved.[9,20–23] From calculations performed, internal reflection measurements are the most sensitive to changes in p. Also, for smaller ratios of thickness to mean free path and for longer wavelengths, electron surface scattering has a greater effect on the optical properties of FEM films. This suggests that determination of the microscopic parameters could be carried out from optical measurements alone. This theory could be tested by using such a determination and Fuch's[29] expression to calculate the conductivity of the film. Comparison of this theoretical value with an experimental value could provide a simple check of the theory's accuracy.

APPENDIX

A thin film of thickness, d, with its first surface the $x-y$ plane, at $z=0$, and its second surface at $z=d$, has electromagnetic radiation incident upon it in the form of an electric field $E(z)e^{\iota\omega t}$, pointing in the x direction, and a magnetic field $H(z)e^{\iota\omega t}$, pointing in the y direction. (The time dependence will be omitted from further expressions.)

Under these conditions, Maxwell's equations are

$$-\frac{dH}{dz}=\frac{\iota\omega E}{c}+\frac{4\pi J}{c} \tag{A1}$$

and

$$\frac{dE}{dz}=-\frac{\iota\omega H}{c} \ , \tag{A2}$$

where $J=J(z)$ is the current density. The second-order differential equation obtained by eliminating H is

$$\frac{d^2E}{dz^2}+\frac{\omega^2E}{c^2}=\frac{4\pi\iota\omega J}{c^2} \ . \tag{A3}$$

Further progress is dependent on finding some relation between J and E. Such a relation was developed by Reuter and Sondheimer.[4] Their development started with a distribution function

$$f=f_0+f_1(\vec{v},z) \ , \tag{A4}$$

where f_0 is the Fermi function and f_1 is an unknown function of $\vec{v}$ and z which is to be determined. Since a steady-state situation will exist, the distribution function is determined by the Boltzmann transport equation

$$\frac{\partial f}{\partial t}-\frac{2\pi e}{h}\left(\vec{E}+\frac{1}{c}\vec{v}\times\vec{H}\right)\cdot\nabla_k f+\vec{v}\cdot\nabla_r f$$

$$=-\frac{f-f_0}{\tau} \ , \tag{A5}$$

where $h\vec{k}=2\pi m\vec{v}$ and $\vec{r}$ is the space vector. Neglecting the product of E and f_1 and H gives the result

$$\frac{\partial f_1}{\partial z}+\frac{1+\iota\omega\tau f_1}{\tau v_z}=\frac{e}{mv_z}\frac{\partial f_0E}{\partial v_x} \ . \tag{A6}$$

The general solution of Eq. (A6) is

$$f_1=\exp\left(-\frac{(1+\iota\omega\tau)z}{\tau v_z}\right)\left[F(v)+\frac{e}{mv_z}\frac{\partial f}{\partial v_x}\int_0^z E(t)\exp\left(\frac{1+\iota\omega\tau}{\tau v_z}\right)dt\right] \ , \tag{A7}$$

where $F(v)$ is an arbitrary function determined by boundary conditions. The only difference between the results Reuter and Sondheimer[4] had and those used in this paper is the electrons can not travel beyond the edges of the film. So $0\leqslant z\leqslant d$ and this must be remembered for several integrations which are performed. The limits on the integrations will be d rather than ∞, as they are for a semi-infinite mass.

The current density is calculated by

$$J(z)=-2e\left(\frac{m}{h}\right)^3\int\int\int v_x f\,dv_x\,dv_y\,dv_z \ , \tag{A8}$$

which results in

$$J(z)=\frac{2\pi e^2m^2v^2}{h^3}\left[p\int_{-d}^{0}k_a\left(\frac{z-t}{l}\right)E(t)\,dt+\int_0^d k_a\left(\frac{z-t}{l}\right)E(t)\,dt\right] \ , \tag{A9}$$

where $a=\omega\tau$, l is the mean free path of the electrons, and

$$k_a(u)=\mathrm{Ei}_1\{(1+\iota a)|u|\}-\mathrm{Ei}_3\{(1+\iota a)|u|\} \ , \tag{A10}$$

with

$$\mathrm{Ei}_n(u)=\int_1^\infty\frac{e^{-su}}{s^n}\,ds \ , \quad \mathrm{Re}(u)>0 \ . \tag{A11}$$

The use of Eq. (A9) in Eq. (A3) gives the basic equation of the problem

$$\frac{d^2E}{dz^2}+\frac{\omega^2E}{c^2}=\frac{8\pi^2\iota\omega e^2m^2v^2}{c^2h^3}\left[p\int_{-d}^{0}k_a\left(\frac{z-t}{l}\right)E(t)\,dt+\int_0^d k_a\left(\frac{z-t}{l}\right)E(t)\,dt\right] \ . \tag{A12}$$

This second-order integro-differential equation may be put in a convenient dimensionless form for analysis, as is Eq. (1).

[1] W. J. Anderson and W. N. Hansen, J. Electrochem. Soc. 121, 1570 (1974).

[2] W. J. Anderson and W. N. Hansen, J. Electroanal. Chem. 47, 229 (1973).

[3] W. N. Hansen (unpublished).

[4] G. E. H. Reuter and E. H. Sondheimer, Proc. R. Soc. London Sect. A 195, 336 (1948).

[5] T. Holstein, Phys. Rev. 88, 1427 (1952).

[6] R. B. Dingle, Physics (N.Y.) 19, 311 (1953).

[7] R. B. Dingle, in Ref. 6, p. 348.

[8] R. B. Dingle, in Ref. 6, p. 729.

[9] R. B. Dingle, in Ref. 6, p. 1187.

[10] H. P. Van de Braak and L. J. M. Van de Klundert, Physica (Utrecht) 77, 532 (1974).

[11] F. J. Tischer, Appl. Phys. 5, 285 (1974).

[12] B. N. Libenson and V. V. Rumyantsev, Phys. Status Solidi B 65, 281 (1974).

[13] F. J. Tischer, Surf. Sci. 44, 411 (1974).

[14] F. J. Tischer, J. Appl. Phys. 45, 2356 (1974).

[15] G. Brandli, Phys. Rev. B 9, 342 (1974).

[16] F. J. Tischer, Proc. IEEE 62, 635 (1974).

[17] F. J. Tischer, Phys. Lett. A 47, 231 (1974).

[18] H. Scher, Phys. Rev. B 3, 3551 (1971).

[19] J. M. Keller, R. Fuchs, and K. L. Kliewer, Phys. Rev. B 12, 2012 (1975).

[20] A. R. Melnyk and M. J. Harrison, Phys. Rev. B 2, 851 (1970).

[21] W. E. Jones, K. L. Kliewer, and R. Fuchs, Phys. Rev. 178, 1201 (1969).

[22] A. R. Melnyk and M. J. Harrison, Phys. Rev. Lett. 21, 85 (1968).

[23] N. J. Takimoto, J. Phys. Soc. Jpn. 25, 390 (1968).

[24] N. J. Takimoto, J. Phys. Soc. Jpn. 34, 1503 (1973).

[25] N. J. Takimoto, J. Phys. Soc. Jpn. 36, 1029 (1974).

[26] W. N. Hansen, J. Opt. Soc. Am. 58, 380 (1968).

[27] F. E. Hutchinson and W. N. Hansen Phys. Rev. B 20, 4076 (1979) (following paper).

[28] M. L. Theye, Phys. Rev. B 2, 3060 (1970).

[29] K. Fuchs, Proc. Cambridge Philos. Soc. 34, 100 (1938).