Frequency dependence of the Drude relaxation time in metal films*

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A two-carrier model is used to explain the frequency dependence of the Drude relaxation time that has been observed in recent experiments on gold films. One carrier is the electrons that exist in the crystallites, regions of high order; the other is the electrons in grain boundaries, regions of low order. This model gives the same dependence on the annealing of the sample as has been seen in the data of Thèye.

I. INTRODUCTION

For a number of years, it has been realized that, in order to fit the infrared optical data on a variety of metals, the Drude theory must be slightly modified by allowing the relaxation time to be frequency dependent. In terms of this parameter τ, the dielectric constant $\tilde{\epsilon} = \epsilon_1 + i\epsilon_2$ is

$$\epsilon_1 = 1 - \frac{\omega_p^2}{\omega^2 + 1/\tau^2}, \quad \epsilon_2 = \frac{\omega_p^2}{(\omega^2 + 1/\tau^2)\omega\tau}, \quad (1)$$

where $\omega_p^2 = 4\pi Ne^2/m^*$, ω is the frequency of the incident light, N is the density of free carriers, and m^* is the effective mass of the carriers. If one knows $\tilde{\epsilon}$, one can solve for $(1/\tau)_{eff}$ at each frequency and from the experiments[1,2] one generally finds

$$(1/\tau)_{eff} \equiv -\omega\epsilon_2/(\epsilon_1 - 1) = a + b\omega^2. \quad (2)$$

In several experimental papers[2-5] on infrared properties of evaporated noble-metal films, a frequency-dependent relaxation time has been observed. In particular Thèye[2] demonstrated, not only that the relaxation time for thin gold samples has the form given by Eq. (2), but also that the size of the frequency-dependent term is a function of whether or not the sample has been annealed.

There are a number of theories which are capable of giving a frequency dependent term in $(1/\tau)_{eff}$. Hopfield[1] has recently summarized the possible origins of this term in transition metals. He finds three possible sources: (i) Band structure and electron-phonon interaction effects; (ii) electron-electron scattering; and (iii) two-carrier effects. None of these effects explicitly includes a dependence on crystalline order. However in some of the experimental papers[2,4] the authors tentatively accounted for the frequency dependence as being due to electron-electron collisions. It is difficult to see how this effect could be sizable enough in noble metals to account for the large effect seen. It is also difficult, as Thèye herself has pointed out, to account for the large variation of relaxation time with film structure. In this paper we

present a simple version of the two-carrier model which is able to explain the observed dependence of b in Eq. (2) on crystalline order.

II. TWO-CARRIER MODEL

In an evaporated unannealed film there are two regions: (a) the areas in the film where electrons will see a perfect lattice, that is inside crystallites, and (b) the areas between crystallites which are highly disordered. Electrons in the two regions will respond differently to an applied electromagnetic field, so we can regard them as being two different kinds of carriers. The two carriers are therefore separated in real space instead of in momentum space as in Ref. 1.

The electrons in the two regions could, in general, have different number densities, effective masses, and relaxation times. In our model, however, we have let the masses and densities be equal; the most important difference between them is their relaxation times. In the region b, the region of low order, the relaxation time τ_b will be much smaller than in region a, perhaps the time taken for an electron to move only a few lattice constants. τ_b will therefore be independent of the size of the crystallites and of the temperature. τ_a, on the other hand, will depend on both the temperature and, to some extent, on the crystallite size.

In calculating $\tilde{\epsilon}$ we must decide how to treat the local-field problem. In a homogeneous material with no bound charges, the local field is equal to the macroscopic applied field. To the extent that the free electrons dominate in the optical response of a real metal, the same is true in this case. Thus Hopfield, in Ref. 1, calculates $\tilde{\epsilon}$ using a two-carrier model with no local-field corrections. In our model, on the other hand, the sample is not homogeneous, and the local field within a grain boundary can be different from that within a crystallite.

Hunderi[6] has recently used the same physical idea as that described here to discuss observed

absorption peaks in unannealed evaporated films in the visible range. He deduces an effective dielectric constant from a calculation of light scattering by ellipsoidal discs (representing grain boundaries) embedded in the metal. Using his Eq. (7) and (11) we find that for the amount of disorder encountered, and in the visible and near ir, which are the ranges of interest here, the local-field corrections are unimportant. In addition we expect these corrections to be reduced even further in our model for two reasons.

Hunderi's calculation correctly deals with the local fields as long as the grain-boundary dimensions are larger than both atomic dimensions and electron mean free paths. As long as the frequency of the applied field is well below the plasma frequency, as it is here, the electrons will effectively screen an impurity or defect in the metal in much the same way as they would at zero frequency (the Fermi-Thomas result). This screening length will be of the order of atomic dimensions so that the screening produced at a grain boundary will be smeared over a length of this size. For very thin grain boundaries the two sides are so close that polarization layers involved in the screening of each side will overlap. The full polarization charge given by the Lorentz-Lorenz value will not develop and local-field corrections will be correspondingly reduced.

Another effect, which also reduces local-field corrections in an imperfect metal, is the fact that the electric fields acting on an electron must be averaged over the path which the electrons follow between collisions.[7] All that matters in calculating absorbed energy is the change in drift velocity between collisions due to the applied field. Since a large fraction of the collisions involve electrons coming from deep within a crystallite and scattering in the grain boundary, over most of the path the important electric field is that appropriate for a grain, not a grain boundary.

Given that we are allowed to ignore local-field corrections, we can perform an extremely simple calculation of $\tilde{\epsilon}$, merely by adding the responses of the two carriers. We find

$$\tilde{\epsilon} = 1 - \frac{4\pi N_a e^2}{m_a^*(\omega^2 + i\,\omega/\tau_a)} - \frac{4\pi N_b e^2}{m_b^*(\omega^2 + i\,\omega/\tau_b)} \ . \quad (3)$$

By taking the real and imaginary parts of this $\tilde{\epsilon}$ we can solve for an effective relaxation time as was done in Eq. (2),

$$\left(\frac{1}{\tau}\right)_{\mathrm{eff}} = \frac{1}{\tau_a}\left[1 + \frac{B}{A}\left(\frac{\omega^2 + \tau_a^{-2}}{\omega^2 + \tau_b^{-2}}\right)\right]^{-1}$$
$$+ \frac{1}{\tau_b}\left[1 + \frac{A}{B}\left(\frac{\omega^2 + \tau_b^{-2}}{\omega^2 + \tau_a^{-2}}\right)\right]^{-1}, \quad (4)$$

where $A = 4\pi N_a e^2/m_a^*$ and $B = 4\pi N_b e^2/m_b^*$. If $\omega\tau_a \gg 1$

and $\omega\tau_b \ll 1$ or if $\omega\tau_a > 1$, $\omega\tau_b < 1$ and $(2B/A)\,\omega^2\tau_b^2 \ll 1$ this equation reduces to

$$(1/\tau)_{\mathrm{eff}} \cong 1/\tau_a + (B/A)\,\tau_b\,\omega^2 \ . \quad (5)$$

If $m_a^* = m_b^*$ then $B/A = N_b/N_a$.

We see that our calculated expression for $(1/\tau)_{\mathrm{eff}}$ has the same form as Eq. (2) which was determined from experiment. The constant term is what one would expect if the sample were a single crystal with only one kind of carrier. This term, however, will differ slightly from film to film. Most of the value of τ_a will come from effects not having to do with defects, i.e., scattering from phonons. If local defects are introduced, however, the frequency of scattering will increase. Thus an annealed film having few defects will have a slightly longer τ_a than an unannealed film. We determine $1/\tau_a$ for each film by taking the extrapolated zero-frequency value of $(1/\tau)_{\mathrm{eff}}$.

The ratio N_b/N_a is determined by the state of crystalline perfection of the sample. Assuming that the microscopic electron densities are equal in the two regions, an approximate value of N_b/N_a can be obtained by estimating an average crystallite size and an average size for the regions between crystallites.

III. COMPARISON WITH EXPERIMENT

In her paper, Thèye gives the average crystallite size for her annealed samples. The lateral dimensions are between 3000 and 5000 Å. She does not give the lateral dimensions for the crystallites in her nonannealed film. We will thus have to estimate their size in order to show that this model yields results that are of the right magnitude to fit the data. We shall assume that the grain boundaries extend for roughly two monolayers into each crystallite (so that the total thickness of this layer is four monolayers or 11.5 Å). This value is close to that chosen by Hunderi.[6]

Now we must decide how to treat the upper and lower surfaces of the film. If they are sufficiently rough and electrons scatter diffusely from them, they have the same physical effect as the disordered regions, and therefore should be considered as contributing to them. On the other hand, if they reflect electrons specularly then the film surfaces play the same role as the ordered regions. Either alternative is possible and could be used in making numerical estimates. Experimental evidence[2-4] tends to support specular reflection even for unannealed films, so we shall assume this here. Thus we can estimate the fractional volume which is disordered (which we take to be equal to N_b/N_a) from the crystallite size estimates.

The parameters for both films are listed in Table I. In order to fit the data for the annealed film, we choose $\tau_b = 0.04 \times 10^{-14}$ sec. This value

TABLE I. Parameters used in calculating the curves of Figs. 1 and 3.

Film	Thickness (Å)	Lateral dimension (Å)	$\left(\dfrac{N_b}{N_a}\right)$	$\left(\dfrac{1}{\tau_a}\right)$(sec^{-1})
Annealed	158	3000	0.0077	0.93×10^{14}
Nonannealed	172	400	0.058	1.18×10^{14}

corresponds to a mean free path of roughly 5 Å. The same value of τ_b is used to fit the data of the nonannealed film. We are obliged to use the exact equation (4), since the behavior of $(1/\tau)_{eff}$ vs ω^2 becomes noticeably nonlinear for this large value of N_b/N_a. In Fig. 1 we plot, along with some of the Thèye data, $(1/\tau)_{eff}$ vs ω^2 for the two films as derived from our model. Notice that both the data and our calculated curve for the nonannealed sample are slightly concave downward. This is therefore a better fit of the data than the purely ω^2 dependence assumed by Thèye.

The reflectance data of Bennett et al.[3,4] also indicate that $(1/\tau)_{eff}$ is frequency dependent. They do not solve for $(1/\tau)_{eff}$ explicitly but only give the reflectance R of their samples as a function of wavelength. However, if one assumes that $(1/\tau)_{eff}$ has the form given by Eq. (5) and substitutes this into Eq. (14) of Ref. 3, one finds that the experimental drop in reflectivity at short wavelengths is very close to the calculated one. Figure 2 shows R as a function of wavelength for two cases (a) $(1/\tau)_{eff} = (1/\tau_0)$ and (b) $(1/\tau)_{eff} = (1/\tau_0) + b\omega^2$. The data shown as well as the value of τ_0 used in the calculations are taken from Bennett and Bennett[3] for their gold sample. We have chosen $b = 0.0015 \times 10^{-14}$ sec. This will give a slightly larger change in $(1/\tau)_{eff}$ than for the unannealed film of Thèye discussed above. Note that the reflectance is almost unchanged due to this frequency-dependent $(1/\tau)_{eff}$ at wavelengths longer than 5 μ and follows
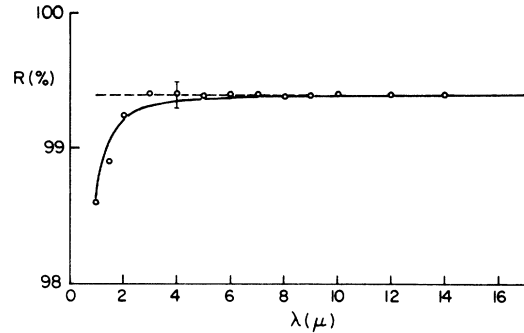
FIG. 2. Reflectivity vs wavelength for gold with parameters taken from Ref. 3. $\tau_0 = 2.46 \times 10^{-14}$ sec, $\sigma_0 = 3.68 \times 10^{17}$ sec^{-1}; (a) dashed curve $(1/\tau)_{eff} = (1/\tau_0)$, (b) solid curve $(1/\tau)_{eff} = (1/\tau_0) + (.0015 \times 10^{-14}$ sec$)\omega^2$. Data taken from Fig. 3 of Ref. 3. Stated error is shown by error bar at 4 μ.

the measured values reasonably well at shorter wavelengths.

This calculation is intended to show that our model is capable of giving a reflectivity curve of the same shape and with roughly the same deviations from the simple Drude result as seen in the experiment. Without knowing in detail the crystallite sizes, nothing more quantitative can be said.

The work of Motulevitch and Shubin[5] also indicates a large ω^2 dependence to $(1/\tau)_{eff}$. In this case they did anneal their sample. However, the gold was not deposited in an ultrahigh vacuum. It has been shown by Bennett and Bennett[3] that there is a 1% increase in reflectivity of gold if deposited in ultrahigh vacuum rather than in a standard vacuum. It could be that the residual gas surrounding the sample during deposition is responsible for preventing it from annealing properly by creating a large number of defects and pinning grain boundaries.

IV. DISCUSSION AND SUMMARY

Hopfield[1] has pointed out that in general electron-electron collisions do not contribute to optical absorption since only collisions that change the total momentum of the electrons will be observable. These collisions will change the total momentum, however, if the Fermi surface is not spherical or if there is a large amount of umklapp scattering. In addition, when in the anomalous skin effect regime, scattering from the sample surface can act, as does umklapp scattering, to allow electron-electron collisions to become effective in changing the total electronic momentum. The equation due to Gurzhi[8] for the frequency of these collisions is used by Bennett et al. [Eq. (25) of Ref. 4] for their work on silver. This equation represents an upper limit to the effect since it represents the total relaxation rate due to electron-electron collisions regardless of whether or not electron momentum
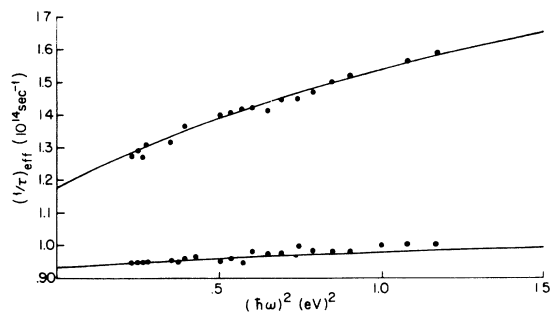
FIG. 1. $(1/\tau)_{eff}$ vs $(\hbar\omega)^2$ as given by Eq. (4). (a) Upper curve is for nonannealed sample of Ref. 2., (b) lower curve is for the annealed sample. The parameters used to calculate these curves are given in Table I. Data taken from Fig. 6 of Ref. 2.

is conserved in the collisions. This corresponds to either a large umklapp probability (appropriate for transition metals) or the extreme anomalous skin effect regime (which occurs for longer relaxation times than those dealt with here). Furthermore, even this upper limit gives a deviation from the simple Drude theory that is roughly six times smaller than the observed values in the gold films discussed above, and, in addition, should not change with sample annealing.

Since grain ooundaries can be thought of as surfaces internal to the sample, it is possible that they will play the same physical role as the external surface. They will then increase the effect of electron-electron scattering in the way predicted by Gurzhi. Clearly, anyone attempting to measure the anomalous skin effect, as for instance derived in the papers by Kliewer and Fuchs,[9] must be careful to know the amount of surface in the sample. In an unannealed film, the effective surface area, the external surface plus the grain boundaries, can be more than twice the external surface area.

There is one additional reason for determining the origin and size of the ω^2 term in $(1/\tau)_{eff}$. In studying the band structure of solids one often looks at the interband contribution to $\tilde{\epsilon}$, calculated by subtracting the extrapolated Drude term from the measured dielectric constant. It therefore becomes important to understand how to treat $(1/\tau)_{eff}$ at high frequencies in the interband region. Our model predicts that as the frequency increases $(1/\tau)_{eff}$ will approach a constant. Electron-electron scattering, on the other hand, predicts $(1/\tau)_{eff}$ will continue to increase as ω^2. Figure 3 shows $(1/\tau)_{eff}$ over a wide frequency range for the same two samples shown in Fig. 1. In the uv we see that $(1/\tau)_{eff}$ for an unannealed film can be more than twice as large as for an annealed one. The Drude contribution to ϵ_2 in the uv would likewise be twice as large as expected from either a resistivity measurement of $(1/\tau)_{eff}$ or from measurements taken from annealed samples.

In conclusion let us remark that if our model is physically correct it provides an accurate method for measuring the degree to which the film surfaces scatter electrons specularly or diffusely — a parameter that is needed in calculating the anomalous skin effect. By looking at the frequency-dependent part of $(1/\tau)_{eff}$ as a function of film thickness and annealing we will know whether the surfaces must be included along with the grain boundaries as regions of high scattering probability.

We have presented a model of free carrier absorption that relies on having two kinds of current carriers within the crystal. Since one type of carrier exists in grain boundaries, the degree of crystallinity of the sample automatically becomes
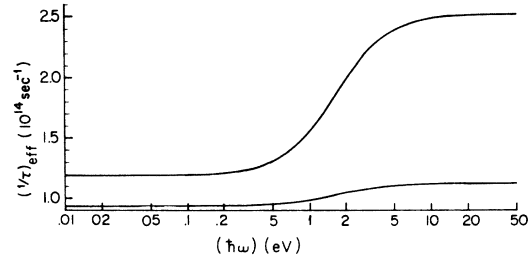

FIG. 3. $(1/\tau)_{eff}$ vs frequency computed in our model using the same parameters as were used in Fig. 1.

important for computing the total number of such carriers. The results derived from this model are in good agreement with present data on noble metal films: in particular the date of Thèye agree with the predicted changes with sample annealing. The only other explanation suggested so far, electron-electron scattering, yields an effect that is much smaller and most importantly one that would not change with sample annealing. It would be interesting to test this model by measuring the infrared optical properties of different metals to see how $(1/\tau)_{eff}$ or reflectivity depends on sample annealing and temperature. Finding an anomalously large and frequency-independent Drude contribution to the uv spectra of unannealed films would likewise indicate the validity of our approach.

In a recent paper,[10] Bernland, Hunderi, and Myers reported anomalously large absorption in films of aluminum evaporated onto cold substrates. The shape of the observed absorption does not correspond to a simple Drude model, as it does for liquid aluminum, and the authors proposed tentative explanations involving modified interband transitions with which they, themselves, were unsatisfied. We wish to point out that our two-carrier model fits the observed absorption quite well with the following parameters: $\tau_a = 3.4 \times 10^{-15}$ sec, $\tau_b = 0.18 \times 10^{-15}$ sec, and $B/A = 1.5$. These results show that our model can be used to describe other metals besides gold, higher photon energies, and very large volume fractions (60%) of disordered material. It thus seems reasonable that this approach can be a useful aid in the study of amorphous materials.

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