

## Effect of liquids on the Drude dielectric function of Ag and Au films

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Spectroscopic ellipsometric measurements were made of the free-electron dielectric functions of Ag and Au films in air and immersed in dielectric liquids of different refractive indexes. The effects seen by Gugger *et al.* were reproduced for Ag and Au films prepared similarly to theirs, and in Ag films with larger grains. Different effects were seen with an (oxidized) single crystal of Ag and a single crystal of Au. The "anomalous" data could be fitted with an effective-medium model by assuming that the liquid penetrates all, or most, of the intergrain regions within the optical penetration depth. The dielectric functions of "ideal" Ag and Au samples were obtained from fits with an effective-medium model.

### INTRODUCTION

Gugger *et al.*<sup>1</sup> recently reported a remarkable, apparently nonlocal, interaction between the conduction electrons in silver and a dielectric liquid in contact with one surface of the Ag film. They measured the dielectric function of two semitransparent Ag films by an attenuated total reflectance technique. These were fitted to the Drude expression<sup>2</sup> for a free-electron gas

$$\epsilon = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2} + \frac{i\omega_p^2}{\tau\omega^3} = \epsilon_1 + i\epsilon_2, \quad (1)$$

valid for  $\omega\tau \gg 1$ . They obtained values of the three parameters;  $\epsilon_{\infty}$ , the contribution to  $\epsilon_1$  from transitions at higher energies (core polarization);  $\omega_p$ , the plasma frequency ( $\omega_p^2 = 4\pi Ne^2/m$ , with  $N$  the electron density); and  $\tau$ , the scattering time. A better fit to the  $\epsilon_2$  data for noble metals can be achieved by using<sup>3-10</sup>

$$\tau^{-1} = \tau_0^{-1} + \beta\omega^2. \quad (2)$$

This probably is best considered an empirical expression at this time because experimental values of  $\beta$  and its temperature dependence do not often agree well with theoretical values. A frequency-dependent  $\tau$  requires that  $\omega_p$  be frequency dependent in order to retain Kramers-Kronig consistency (causality), although the frequency dependences of  $\tau$  and of  $\omega_p$  need not occur in the same spectral region. Gugger *et al.* then immersed each film in a liquid of different refractive index and repeated the measurements. From the dielectric functions obtained for the Ag (with consideration of the liquid's refractive index in the Fresnel equations), they found values of  $\tau_0$  and  $\omega_p$  which were larger than those obtained without the liquid and values of  $\beta$  which were smaller. They concluded tentatively that this was a genuine microscopic effect; the properties of the conduction electrons within the metal and/or their scattering at the interface depend on the refractive index of the adjacent liquid.

Weber<sup>11</sup> suggested that the effect arose from the neglect of a contamination layer on the air-exposed films. Gugger *et al.* responded<sup>12</sup> that consideration of such a layer

modified the parameters, but still left the changes described above. In the following we use a different measurement technique, ellipsometry, and opaque films, to verify the data of Gugger *et al.*<sup>1</sup> for Ag, and show a similar effect for Au. We then show that the effect also occurs for a film evaporated on a hot substrate, i.e., a film with larger crystallites. We show that the effect of a liquid is different for single-crystal surfaces of Ag and Au. These results strongly suggest that the liquid penetrates the grain boundaries to some extent. We model this an effective medium and find a good fit to the data. Thus, there is no need for an interaction between the liquid and the conduction electrons to explain the data.

### EXPERIMENTAL PROCEDURE

The optical measurements were made on a spectroscopic ellipsometer.<sup>13-16</sup> The radiation source was a 75-W Xe arc or a W-filament lamp and a 0.25-m monochromator with interchangeable diffraction gratings. The detector was one of two end-window photomultipliers, one with an S-1 cathode having been used in the work reported below. This ellipsometer differs from most others in that both polarizer and analyzer were rotated, at  $\Omega$  and  $2\Omega$ , respectively. The amplitudes of the photomultiplier output at  $\Omega$ ,  $2\Omega$ , and  $3\Omega$  were used to obtain  $\epsilon_1$  and  $\epsilon_2$ . (In obtaining them, a correction was applied for the refractive index of the medium above the surface of the film.) This type of ellipsometer does not require the measurement of any dc outputs, so the large dark current from the S-1 cathode contributed only noise, not a correction to the measured signal. A fused SiO<sub>2</sub> quarter-wave retarder<sup>17-20</sup> (AD-2 of Ref. 20) was used to reduce the polarization effects of the monochromator. The angle of incidence on the sample was 68°.

Samples were opaque films of 99.99% pure Ag or Au evaporated at a rate of 60–90 Å/s at a pressure of  $10^{-6}$  Torr onto quartz substrates held at room temperature or at 350 °C. Thicknesses ranged from 1700–2700 Å. A Ag(100) single-crystal face, polished, then chemically polished,<sup>21</sup> and a polished, unetched single crystal of Au were also used. Grain sizes were estimated from scanning

electron microscope micrographs to be up to about 10 000 Å for the Ag films condensed on the hot substrates, and up to about 1000 Å for Ag and Au films condensed at room temperature. The samples were held in a cell with fixed windows, whose effect on the measurements was much smaller than the effects studied. The cell was also used for the measurements in air.

The ellipsometer has been used for measurements on several materials during its initial operation phase. Measurements of Au films prepared as above, but on large substrates, were made in the 1.0–5.5-eV spectral region for comparison with the data in the study by Aspnes *et al.*<sup>22</sup> In the region of strong interband transitions, our  $\epsilon_2$  spectra resemble in shape and magnitude those reported by Aspnes *et al.* and by Johnson and Christy<sup>23</sup> for similar films, i.e., films evaporated at modest rates onto room-temperature SiO<sub>2</sub> or NaCl substrates. The magnitude of interband  $\epsilon_2$  spectra for our films indicated a volume fraction of voids of about 5%, close to what we obtained from the present study of the Drude region.

The procedure for measurements was to make six or seven films at the same time. Each was measured in air. If any one film had an apparent dielectric function significantly different from the others, it was rejected. (This sometimes happened for films on substrates mounted at one side of the bell jar, with the atomic beam incident far from normal.) The apparent dielectric functions, measured in air, of all the films used fell on the same line in Figs. 1(a) and 2(a). Scatter among films prepared simultaneously was far less than the effects observed by covering the surfaces with liquids. Each film was then measured when immersed in one liquid. The liquids used were water ( $n = 1.33$ ), toluene ( $n = 1.51$ ), and fluorocarbons with refractive indexes of 1.42 and 1.60.<sup>24</sup> Some of the films were allowed to dry and were then remeasured in air. All the films evaporated onto room-temperature substrates were altered by the immersion in liquid, for the resultant apparent dielectric function after drying was always between that obtained originally in air and that obtained under immersion. The failure to “dry out” precluded using one film for more than one immersion. Films evaporated onto a substrate at 350°C and the single crystals had their original dielectric functions when remeasured after air drying. In obtaining  $\bar{\epsilon}$  from the measurements, the dispersion of the refractive indexes was considered. The liquid of refractive index 1.60 was not stable in air and gradually turned yellow upon use. Fresh liquid was used frequently, but some errors appeared to arise from the aging of this liquid.

From the measured  $\epsilon_1$  and  $\epsilon_2$ , we obtained the Drude parameters following the analysis of Gruger *et al.* The relaxation time  $\tau$  was obtained as  $\tau^{-1} = \omega\epsilon_2 / (\epsilon_\infty - \epsilon_1)$ .  $\epsilon_\infty$  and  $\omega_p$  were obtained from a least-squares fit of  $\epsilon_1$  vs  $\lambda^2$ . Least-squares fits of  $[\tau(\omega)]^{-1}$  vs  $\omega^2$  gave  $\tau_0$  and  $\beta$ .

Our measurements differ from those of Gugger *et al.* in two principal ways. First, a different measurement technique was used. Second, the liquid-metal interface in our case was the interface of incidence, where the fields of the measuring beam are larger than at the interface used by Gugger *et al.* If there is a real microscopic effect, it should be more prominent.

## RESULTS

Figure 1(a) shows  $\epsilon_1$  versus  $\lambda^2$  for Ag films evaporated on a room-temperature substrate immersed in liquids of different refractive indexes. Some data from Gugger *et al.* are also shown. A similar effect was obtained for Au

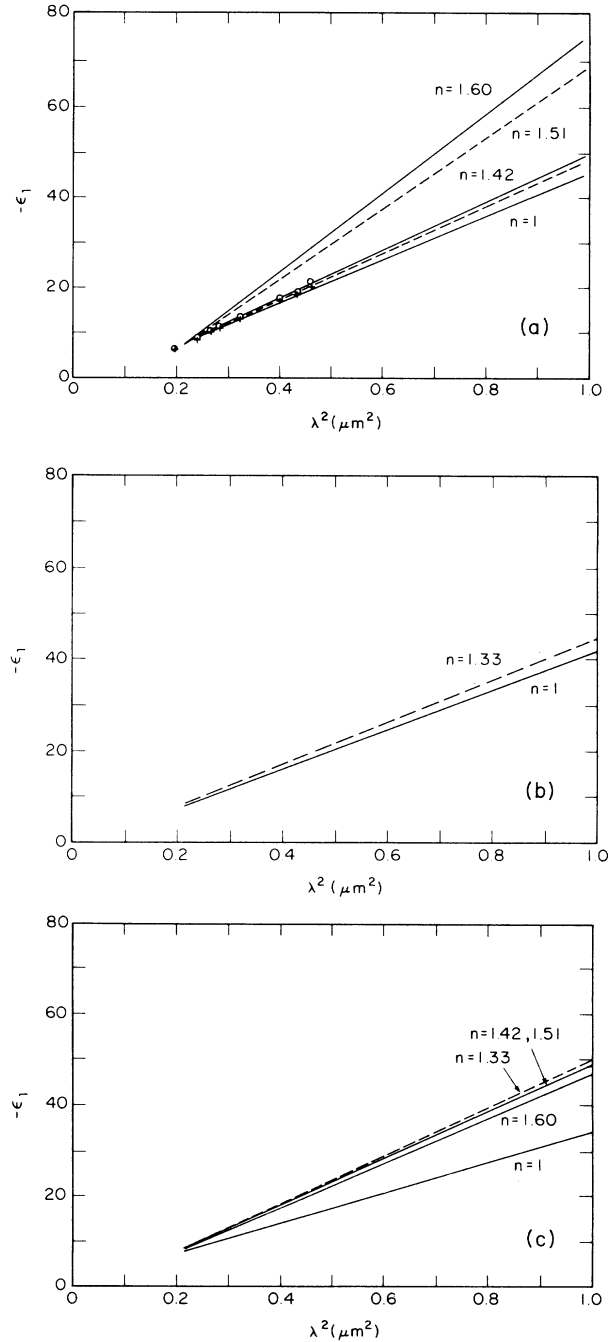


FIG. 1. Real part of the apparent dielectric function of Ag vs the square of the wavelength for samples measured in fluids of different refractive indexes, as indicated. (a) Films condensed on substrates at room temperature. The circles and crosses are data on two films from Gugger *et al.* (Ref. 1), measured in air. (b) Film condensed on a substrate at 350°C. (c) A single crystal.

films evaporated on a room-temperature substrate. Similar data are shown in Figs. 1(b) and 1(c) for Ag films evaporated on 350°C substrates and for a single crystal of Ag, respectively. It is obvious that the effect of the liquid

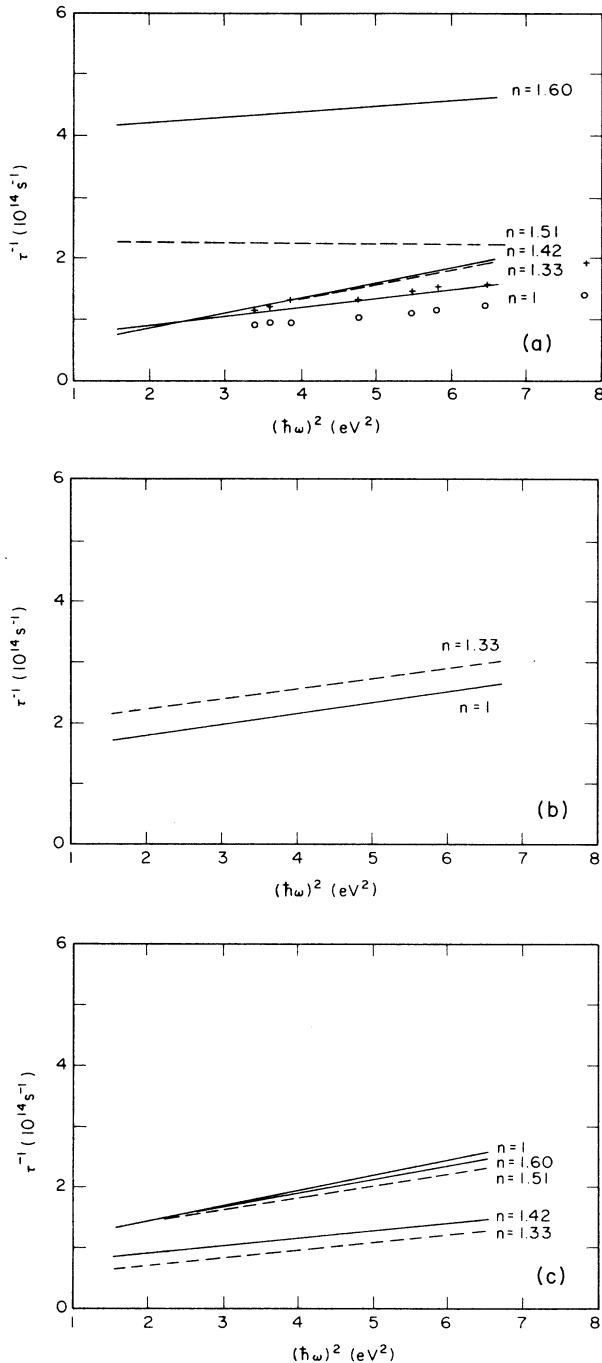


FIG. 2. Apparent scattering rate for Ag, determined from the imaginary part of the apparent dielectric function, vs the square of the photon energy for samples measured in fluids of different refractive indexes, as indicated. (a) Films condensed on substrates at room temperature. The circles and crosses are data on two films from Gugger *et al.* (Ref. 1), measured in air. (b) Film condensed on a substrate at 350°C. (c) A single crystal.

is similar for the smaller-grained films of Fig. 1(a) and the larger-grained film of Fig. 1(b). The effect of the liquid is not monotonic with increasing liquid refractive index for the single crystal of Ag and for the single crystal of Au (not shown).

The scattering rate,  $\omega\epsilon_2/(\epsilon_\infty - \epsilon_1)$ , is plotted similarly in Fig. 2. The data shown in both Figs. 1 and 2 are least-squares fits to the measured spectra, which consist of points taken every 0.01 eV. The random scatter about the fitted lines is small compared to an oscillation of the data about the lines, of the order of 25% in  $\tau^{-1}$  and a few percent in  $\epsilon_1$  which we believe to be genuine, not an instrumental effect. It is roughly periodic in  $(\hbar\nu)^2$ , and can be seen in the data of Parkins *et al.*<sup>25</sup> for Cu, Ag, and Au. This will be reported separately.

The parameters extracted from the least-squares fits are shown in Table I. The data for the Ag single crystal measured in air are unphysical in that  $\epsilon_\infty$  is negative and  $\omega_p$  is too low. Upon immersion in liquids, more reasonable values are obtained. The reason for this is that the Ag surface probably is still covered with a film of oxide, because the chemical polish consists of an oxidation in the first solution, followed by reduction of the oxide in the second. Silver oxides should be transparent in our spectral regions, with a refractive index of 1.4–2.0. Thus, to extract the true Drude parameters, we should model the material as silver covered with an oxide layer, not as bulk silver. Upon immersion in any liquid, a better impedance match is achieved and the effect of the overlayer is diminished. Because of such a layer, one could argue that the interaction between the conduction electrons and the liquid is diminished by the intervening oxide layer, but we believe our case does not rest on the single-crystal data alone. [We can estimate the oxide thickness by comparing the ellipsometric results for the crystal measured in air with those expected for clean bulk Ag (using  $\epsilon_A$  below) using an expression from Ref. 15. The result is that  $d(\text{\AA}) = 35n^2/(n^2 - 1)$ , with  $n$ , the oxide refractive index. If  $n = 1.41$ ,  $d = 70 \text{\AA}$ .]

The gold films show an effect from the ambient liquid similar to that of Ag films, an increase in  $\omega_p$  and a decrease in  $\beta$  as the refractive index of the liquid increases, the same effect observed by Gugger *et al.*<sup>1</sup> The Au single crystal shows parameters that shift nonmonotonically with liquid refractive index, as did those of the Ag crystal. A film of  $\text{Au}_2\text{O}_3$  can account qualitatively for this effect, but  $\text{Au}_2\text{O}_3$  absorbs.<sup>26</sup> Its dielectric function is not known below 1.5 eV, making an estimate of the film thickness difficult.

## DISCUSSION

Our data can be explained by the presence of grain boundaries, which can be infiltrated by the liquid. The outer region or the entire film should then be viewed as a composite medium, modeled below. The medium consists of Ag and a fluid, either air or a liquid. The changes in the optical properties of this layer due to using a fluid with a different refractive index account for the observed changes in the apparent dielectric function, or pseudo-dielectric-function  $\langle \epsilon \rangle$  of the assumed homogeneous sample. After removal from the liquid, not all of the liquid

TABLE I. Apparent Drude parameters for immersed silver and gold.

Sample	Nominal refractive index of fluid	$\epsilon_\infty$	$\omega_p^2$ ( $10^{32} \text{ s}^{-2}$ )	$\tau_0$ ( $10^{-14} \text{ s}$ )	$\beta$ ( $10^{14} \text{ s}^{-1} \text{ eV}^{-2}$ )
Ag (film, room-temperature substrate)	1.00	2.63	1.738	1.66	0.150
	1.33	3.13	1.857	2.39	0.229
	1.42	3.64	1.924	2.66	0.246
	1.51	9.74	2.828	0.44	-0.005
	1.60	11.31	3.142	0.25	0.090
Ag (film, 350°C substrate)	1.00	1.20	1.552	0.702	0.181
	1.33	1.31	1.646	0.535	0.170
Ag (single crystal)	1.00	-0.582	1.220	1.03	0.244
	1.33	2.878	1.918	2.20	0.124
	1.42	3.022	1.878	1.51	0.123
	1.51	2.573	1.787	0.934	0.188
	1.60	3.283	1.840	1.35	0.229
Au (film, room-temperature substrate)	1.00	7.76	1.651	1.618	0.187
	1.33	8.71	1.846	1.323	0.160
	1.42	9.17	1.905	1.072	0.083
	1.51	9.65	1.976	0.997	0.090
	1.60	10.30	2.039	0.676	0.011
Au (single crystal)	1.00	6.14	1.468	1.277	0.203
	1.33	7.87	1.785	1.206	0.184
	1.42	7.84	1.784	0.998	0.240
	1.51	9.18	2.004	0.974	0.129
	1.60	10.07	2.099	0.763	0.155

may leave the region between grains and the optical properties do not return completely to their original values. It is possible that when the liquid penetrates along the grain boundaries, it does not displace all of the air in the grain boundaries, in which case, we must consider a three-component composite medium. There should be a greater volume of grain boundary in the films evaporated onto room-temperature substrates than in those evaporated on substrates at 350°C. The single-crystal surfaces should have no grain boundaries, but in our case, they are covered with an oxide layer of unknown morphology.

We first modeled the system the following way. We assumed that the entire region of the film sampled (the optical penetration depth is only 100–140 Å) is a composite medium, composed of a volume fraction  $f_A$  of silver of dielectric function  $\tilde{\epsilon}_A$  and a volume fraction  $f_B$  of fluid of known real dielectric function  $n^2$ , with  $f_A + f_B = 1$ . We cannot use our crystal data for  $\tilde{\epsilon}_A$  because of the oxide layer, and we chose not to use literature values, the best of which in our spectral region may be those of Winsemius.<sup>27</sup> We thus treated  $\tilde{\epsilon}_A$  as unknown. We measured  $\langle \tilde{\epsilon} \rangle$ . We used the Bruggeman effective-medium model,<sup>28</sup> shown by Aspnes *et al.*<sup>29</sup> to be the most appropriate. This model treats both components on an equal footing, neither one being the host for the other. The host is the effective medium. The dielectric functions are related by

$$f_A \frac{\tilde{\epsilon}_A - \langle \tilde{\epsilon} \rangle}{\tilde{\epsilon}_A + 2\langle \tilde{\epsilon} \rangle} + f_B \frac{n^2 - \langle \tilde{\epsilon} \rangle}{n^2 + 2\langle \tilde{\epsilon} \rangle} = 0. \quad (3)$$

The three unknowns were found by evaluating the real and imaginary parts of Eq. (3) twice at each photon energy, once for each of two fluids. The result was a spectrum of  $\tilde{\epsilon}_A$ , the dielectric function for bulk metal, and a value for  $f_B$ , which should be the same for each photon energy. We did this for four data sets from the Ag films evaporated on room-temperature substrates, using the measurements in air and in one liquid for each liquid, and similarly for the one data-set pair for the Ag films evaporated on a substrate at 350°C. The resultant volume fractions were quite wavelength independent, and the Drude parameters for the resultant silver dielectric functions were more nearly the same for all data sets than those in Table I. They still shift with increasing  $n$ , but to a lesser extent than the values in Table I. This suggests that the model, which is physically reasonable, gives a quantitatively better explanation of our data than the use of a homogeneous medium. We could use this  $\tilde{\epsilon}_A$  data in the Bruggeman model and obtain  $\langle \tilde{\epsilon} \rangle$  spectra rather close to all of the data set we measured on the films.

A more realistic model, but with an additional parameter, was then used. It was assumed that the liquid occupied a volume fraction  $f_C$  and the air a volume fraction  $f_B$  within the penetration depth, with  $f_A + f_B + f_C = 1$ . A third term was added to Eq. (3), and the real and imaginary parts of the equation evaluated twice, once for data taken in air and once for data taken with a liquid. Values of  $f_B$  and  $f_C$ , and a spectrum of  $\tilde{\epsilon}_A$ , were obtained. The fit was not sensitive to the individual values of  $f_B$  and  $f_C$ ,

but it was sensitive to their sum, i.e., to  $f_A$ . Only the sum is shown in Table II, along with the Drude parameters obtained from this fit for all Ag and Au films. We present these as our best representation of the dielectric function of pure bulk Ag and Au in this spectral region for our data taken on films. Table II also shows the Drude parameters extracted by Winsemius<sup>27</sup> from his data on bulk polycrystalline samples, those of Beach and Christy<sup>9</sup> extracted from data on Ag films, and parameters we extracted from the data of Aspnes *et al.*,<sup>21</sup> taken on annealed films, which provide the longest relaxation times in the Drude region. The values of  $\omega_p$  and  $\beta$  are plotted in Fig. 3 as a function of the refractive index of the ambient fluid, both before and after using the effective-medium modeling. It is clear that for the Au films the parameters are nearly independent of the refractive index of the fluid upon use of the effective-medium model, and that the dependence upon refractive index is reduced for the Ag films.

A third method of analysis was to assume that the liquid penetrated to a depth  $d$ , but that it completely replaced all the air there. A two-layer model was used, with each layer on effective medium. The volume fraction of liquid in the outermost layer was assumed to be the same as the volume fraction of air in the lower layer. Solutions for  $\bar{\epsilon}_A$ ,  $f_B$ , and  $d$  were very insensitive to the value of  $d$ . They centered on  $d \sim 100$  Å, a reasonable value about the diameter of some of the crystallites and close to the optical penetration depth.

It can be seen from Table II and Fig. 3 that the use of the effective-medium model for the Au films results in essentially constant Drude parameters ( $\omega_p$ ,  $\beta$ ,  $\tau_0$ , and  $\epsilon_\infty$ ) for all data set pairs used. The effect of the analysis is not

as dramatic for the Ag films. The values of  $\beta$  fall with increasing refractive index of the liquid, but only slightly. The increase in  $\omega_p$  with increase in refractive index is still present, but the effect is only half as large in Table II as in Table I. The fractions of the films occupied by air and liquid are also constant for the Au films, while they increase with refractive index of the liquid for the Ag films, an unexpected increase. It is possible that the poorer fit for Ag compared with Au is a result of slight oxidation of the surfaces of the Ag films, the effect of which is lumped in with that of the voids containing fluid in our fit. A slightly smaller fraction of voids appears to be present for the Ag film condensed on the hot substrate, but the fraction is not smaller by as much as might be expected from comparing Figs. 1(a) and 1(b). We expect the large-grained films to contain a smaller volume fraction of voids, but this appears to be compensated by the increase in surface roughness, which, in the model, appears as an increase in void volume. Additional modeling of these data, e.g., treating an oxide layer<sup>11</sup> along with the effective-medium model, was not carried out.

The values of  $\bar{\epsilon}_A$  in Table II were used to calculate  $\langle \bar{\epsilon} \rangle$  for comparison with the measured values. A similar comparison was made for  $\rho$ , the ratio of the reflected fields for  $p$  and  $s$  polarization, one of the two ellipsometric parameters. In this spectral region,  $\rho$  is very close to unity. The results of these fits are shown in Table III.

In the Drude region,  $|\bar{\epsilon}|$  is large and it is not obvious that the Bruggeman effective-medium theory can be used. Granqvist and Hunderi<sup>30</sup> have examined this question. They consider waves reflected and transmitted by an inhomogeneous slab containing independently scattering particles, whose scattering is described exactly by Mie

TABLE II. Drude parameters for bulk Ag and Au from film data.

Sample	Data set	$\epsilon_\infty$	$\omega_p^2$ ( $10^{32}$ s $^{-2}$ )	$\tau_0$ ( $10^{-14}$ s)	$\beta$ ( $10^{14}$ s $^{-1}$ eV $^{-2}$ )	$f_B + f_C$
Ag (30°C substrate)	air, $n = 1.33$	2.94	1.813	1.669	0.107	0.013
	air, $n = 1.42$	3.38	1.861	1.664	0.101	0.017
	air, $n = 1.51$	5.47	2.144	1.667	0.079	0.057
	air, $n = 1.60$	6.65	2.356	1.701	0.074	0.091
Ag (350°C substrate)	air, $n = 1.33$	1.56	1.594	0.705	0.176	0.011
Ag	bulk polycryst. <sup>a</sup>	b	1.77	0.86	b	b
Ag	film <sup>c</sup>	2.4	1.894 <sup>d</sup>	4.65	0.134	b
Au (30°C substrate)	air, $n = 1.33$	8.12	1.762	1.558	0.181	0.043
	air, $n = 1.42$	8.00	1.775	1.661	0.204	0.053
	air, $n = 1.51$	8.23	1.789	1.560	0.181	0.051
	air, $n = 1.60$	8.23	1.765	1.527	0.171	0.039
Au	bulk polycryst. <sup>a</sup>	b	1.690	0.61	0.063	b
	film <sup>c</sup>	8.13	1.79	20.0	0.204	

<sup>a</sup>Data and analysis from Ref. 27.

<sup>b</sup>Not reported.

<sup>c</sup>Data and analysis from Ref. 9.

<sup>d</sup>This gives almost the free-electron effective mass ( $m^* = 0.99$ ).

<sup>e</sup>Data from Ref. 21 and personal communication.

scattering. An effective-medium model can be used if the same refractive index can be used to calculate both the reflectance and transmittance. This requires the (dipole) scattering amplitude to be the same in the forward and backward directions, which leads to the condition

$$\frac{k^2 d^2}{15} \frac{(\bar{\epsilon}+4)(\bar{\epsilon}+2)}{(2\bar{\epsilon}+3)} \ll 1.$$

For  $|\epsilon_1| \gg \epsilon_2$ , this becomes approximately  $k^2 d^2 |\epsilon_1| / 30 \ll 1$ , where  $k$  is the wave vector and  $d$  the diameter of the scatterer. At  $1 \mu\text{m}$  wavelength for Ag, the left-hand side of this inequality is  $0.17 \times 10^{-4} d^2 \text{ \AA}^{-2}$ . Spherical particles smaller than  $85 \text{ \AA}$  in diameter keep the left-hand side less than 0.05, but most of our grains are larger than this, certainly in the case of the films evaporated on hot substrates. This means that higher multipole scattering begins to play a role.

Another problem with interpreting these data for bulk silver is that in the case of the films evaporated on room-temperature substrates, the mean photon penetration depth is of the order of the electron mean free path, which is limited by the small grain size. This means we are in

the weakly anomalous skin effect regime. Motulevich<sup>31</sup> has discussed this case, and the largest effect is an apparent increase in the imaginary part of the free-electron dielectric function. The true  $\epsilon_2$  is approximately equal to the measured  $\epsilon_2$  plus an additive term of

$$\frac{3}{8}(1-p) \frac{v_F \omega_p}{c\omega},$$

with  $p$  the fraction of specular scattering at the surface and  $v_F$  the Fermi velocity. Whenever the grain size is of the order or smaller than the optical penetration depth, a correction for the anomalous skin effect becomes necessary. It is possible that the spread in values for  $\beta$ , discussed in Ref. 1, arises, at least in part, from a spread in grain sizes, which give different corrections to  $\epsilon_2$  varying as  $\omega^{-1}$ . The different dependence on  $\omega$  may not be detectable in the limited  $\omega$  range frequently employed. We applied the maximum correction of this type ( $p=0$ ) to the data for Ag given by the first line in Table II. This correction produced an increase in the value of  $\beta$  of only 3%, not significant in view of expected errors.

This correction does, however, offer a possible explana-

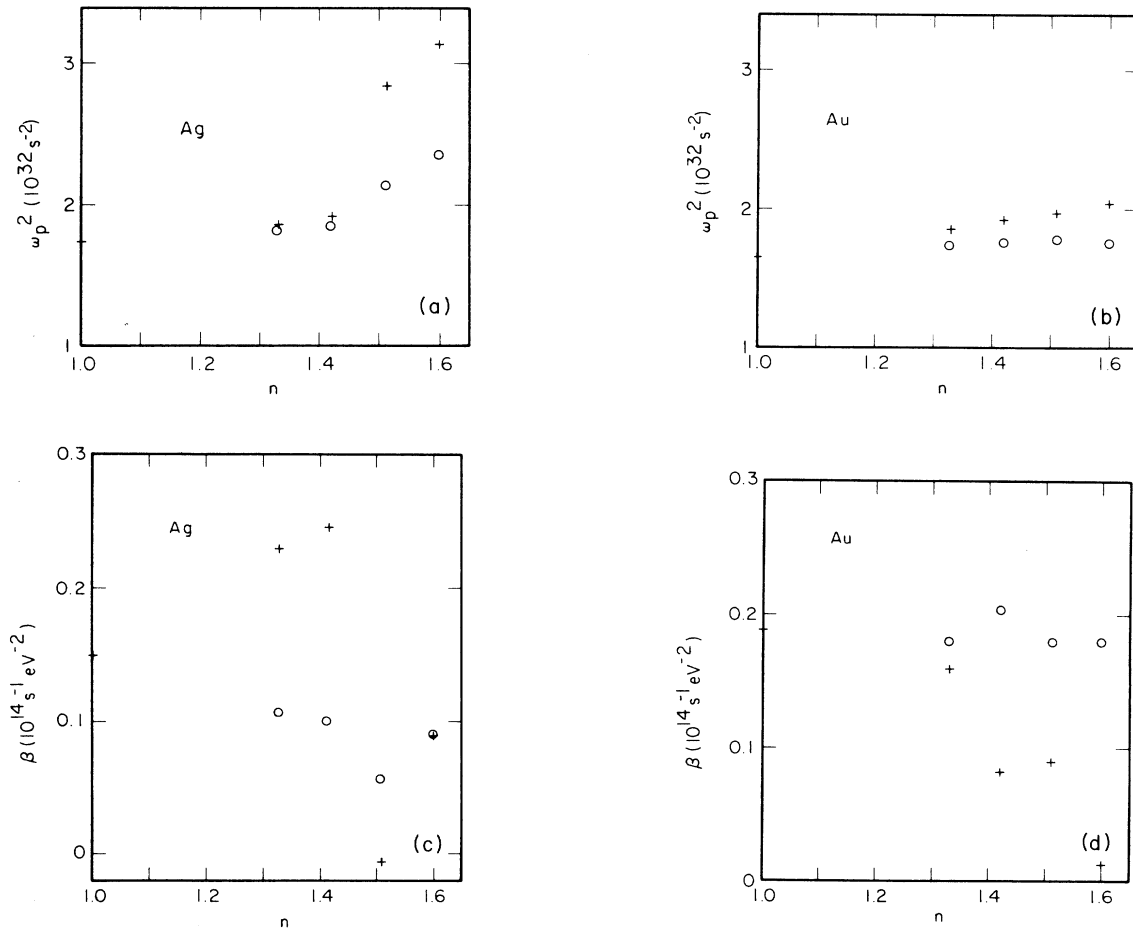


FIG. 3. Drude parameters for Ag and Au films plotted as a function of the refractive index of the ambient medium. The crosses are the original data (Table I) and the circles are the fit for the metal using the Bruggeman effective-medium model (Table II). (a) Plasma frequency for Ag; (b) plasma frequency for Au; (c)  $\beta$  for Ag; (d)  $\beta$  for Au.

tion for the fact that the value of  $\tau_0$  is smaller for the large-grained film than for the smaller-grained one (both measured in air as in Table I, or from Table II). The morphology of the two types of film is very different. In addition to the grain-size difference, the films condensed at high temperatures are much rougher. The surfaces scatter visible light, enough to give then a cloudy cast. Despite this, the ellipsometric results are not so different,<sup>32</sup> except for the values of  $\tau_0$ . If  $p=0$  for the film condensed at 350°C, and  $p=1$  for the films condensed at room temperature, the former will have about half the apparent value of  $\tau_0$  of the latter. It is difficult to assign a value of  $p$ , *a priori*. The difference in surface morphology may alter the effect of the liquid. Both films have nearly the same volume fraction of voids, but they may be quite different in size and shape. The films condensed at room temperature have smooth surfaces and many grain boundaries. Those condensed at 350°C have fewer grain boundaries, but a rough surface, part of which must be included in the region of voids.

### SUMMARY

We have reproduced the effect seen by Gugger *et al.*<sup>1</sup> and have shown that it exists for Au as well. The Bruggeman effective-medium model can reproduce all the measurements on Au in four liquids using a single dielectric function for the metal and a reasonable value for the volume of the film occupied by air or liquid. The fit for Ag is not as good, but it reduces the magnitude of any possible interaction between the liquid and metallic electrons by a factor of 2.

TABLE III. Fit of effective-medium model to measured data ( $\bar{\rho}$ ).

Sample	Data set	$\sigma_p^a$
Ag (30°C substrate)	$n = 1.00$	0.002
	$n = 1.33$	0.005
	$n = 1.42$	0.006
	$n = 1.51$	0.029
	$n = 1.60$	0.072
Au	$n = 1.00$	0.000
	$n = 1.33$	0.002
	$n = 1.42$	0.010
	$n = 1.51$	0.012
	$n = 1.60$	0.014

<sup>a</sup> $\sigma_p$  is given by

$$\sigma_p^2 \equiv \frac{1}{N-2} \sum_{i=1}^N (|\bar{\rho}_i^{\text{expt}}| - |\bar{\rho}_i^{\text{calc}}|)^2.$$

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<sup>1</sup>H. Gugger, M. Jurich, J. D. Swalen, and A. J. Sievers, *Phys. Rev. B* **30**, 4189 (1984).

<sup>2</sup>F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972).

<sup>3</sup>R. N. Gurzhi, *Zh. Eksp. Teor. Fiz.* **35**, 965 (1958) [*Sov. Phys.—JETP* **8**, 673 (1959)].

<sup>4</sup>T. Holstein, *Ann. Phys. (N.Y.)* **29**, 410 (1964).

<sup>5</sup>H. E. Bennett, J. M. Bennett, E. J. Ashley, and R. J. Motkya, *Phys. Rev.* **165**, 755 (1968).

<sup>6</sup>P. B. Allen, *Phys. Rev. B* **3**, 305 (1971).

<sup>7</sup>F. Abeles, in *Optical Properties of Solids*, edited by F. Abeles (North-Holland, Amsterdam, 1972), p. 93.

<sup>8</sup>J. W. Allen and J. C. Mikkelsen, *Phys. Rev. B* **15**, 2952 (1977).

<sup>9</sup>R. T. Beach and R. W. Christy, *Phys. Rev. B* **16**, 5277 (1977).

<sup>10</sup>J. B. Smith and H. Ehrenreich, *Phys. Rev. B* **25**, 923 (1982).

<sup>11</sup>W. H. Weber, *Phys. Rev. B* **34**, 1319 (1986).

<sup>12</sup>H. Gugger, M. Jurich, J. D. Swalen, and A. J. Sievers, *Phys. Rev. B* **34**, 1322 (1986).

<sup>13</sup>D. E. Aspnes, *J. Opt. Soc. Am.* **64**, 639 (1974).

<sup>14</sup>D. E. Aspnes and A. A. Studna, *Appl. Opt.* **14**, 220 (1975).

<sup>15</sup>D. E. Aspnes, in *Optical Properties of Solids: New Developments*, edited by B. O. Seraphin (North-Holland, Amsterdam, 1976), p. 799.

<sup>16</sup>D. E. Aspnes, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, New York, 1985), p. 89.

<sup>17</sup>A. E. Oxley, *Philos. Mag.* **21**, 517 (1911).

<sup>18</sup>V. A. Kizel, Y. I. Krasilov, and V. N. Shamraev, *Opt. Spectrosc. (USSR)* **17**, 248 (1964).

<sup>19</sup>P. B. Clapham, M. J. Downs, and R. J. King, *Appl. Opt.* **8**, 1965 (1969).

<sup>20</sup>J. M. Bennett, *Appl. Opt.* **9**, 2123 (1970).

<sup>21</sup>Alternate immersion in a 1:1 solution of 50 mol % H<sub>2</sub>O<sub>2</sub> and 0.42M NaCN and in a 0.77M aqueous solution of NaCN.

<sup>22</sup>D. E. Aspnes, E. Kinsbron, and D. D. Bacon, *Phys. Rev.* **21**, 3290 (1980).

<sup>23</sup>P. B. Johnson and R. W. Christy, *Phys. Rev. B* **6**, 4370 (1972).

<sup>24</sup>R. P. Cargille Laboratories, Inc., 55 Commerce Rd., Cedar Grove, NJ 07009.

<sup>25</sup>G. R. Parkins, W. E. Lawrence, and R. W. Christy, *Phys. Rev. B* **23**, 6408 (1981).

<sup>26</sup>D. M. Kolb and J. D. E. McIntyre, *Surf. Sci.* **28**, 321 (1971).

<sup>27</sup>P. Winsemius, Ph.D. thesis, Leiden University, 1973.

<sup>28</sup>D. A. G. Bruggeman, *Ann. Phys. (Leipzig)* **24**, 636 (1935).

<sup>29</sup>D. E. Aspnes, J. B. Theeten, and F. Hottier, *Phys. Rev. B* **20**, 3292 (1979).

<sup>30</sup>G. G. Granqvist and O. Hunderi, *Phys. Rev. B* **16**, 3513 (1977).

<sup>31</sup>G. P. Motulevich, *Zh. Eksp. Teor. Fiz.* **46**, 287 (1964) [*Sov. Phys.—JETP* **19**, 199 (1964)].

<sup>32</sup>D. W. Berremann, *J. Opt. Soc. Am.* **60**, 499 (1970).