

Comments

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Comment on "Observation of an index-of-refraction-induced change in the Drude parameters of Ag films"

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It is shown that the recently observed differences in the optical constants of Ag films measured at the metal-air and metal-liquid interfaces by Gugger *et al.* [Phys. Rev. B 30, 4189 (1984)] can be attributed to the presence of the thin contamination layer that forms on a clean Ag film exposed to room air.

In a recent paper Gugger, Jurich, Swalen, and Sievers¹ report the observation of an index-of-refraction-induced change in the optical constants of Ag films. They conclude that, in the free-electron spectral region ($\omega < \omega_p$), the real part of the Ag dielectric constant is more negative, indicating a higher plasma frequency ω_p , when the Ag film is adjacent to a medium with a higher index of refraction. This conclusion is based on a series of surface-plasmon-excitation attenuated-total-reflection (ATR) measurements comparing data on the same film obtained first at an air and then at a liquid interface. They argue convincingly that the observed differences in ω_p cannot be explained by mechanisms involving metal grains, surface roughness, a reduced film density near the surface, or surface-plasmon-assisted absorption. In this Comment, I demonstrate that the observed differences between the results at the two interfaces can be explained by allowing for the thin contaminating layer that forms on the Ag film after exposure to air.

In the following, I estimate the changes in the apparent $\text{Re}(\epsilon_{\text{Ag}})$ produced by the contaminating layer and then show that, when corrected for these changes using suitable layer properties, the systematic differences in the data at the two interfaces nearly disappear. To simplify, I assume that the adlayer is very thin, the Ag film very thick, and ϵ_{Ag} real. The experimental geometry is shown in Fig. 1. The surface-plasmon ATR method consists of measuring $R_p(\theta)$, the reflectivity for *p*-polarized light, and fitting to the multilayer Fresnel formula. There will be a sharp minimum in $R_p(\theta)$ when the incident beam resonantly drives surface plasmons at the metal-air or -liquid interface, the position of which primarily determines $\text{Re}(\epsilon_{\text{Ag}})$. Without the contaminating layer this would occur when

$$(\omega/c)n_p \sin\theta = k_{\text{SP}} \cong (\omega/c)[\epsilon_1 \epsilon_3 / (\epsilon_1 + \epsilon_3)]^{1/2}, \quad (1)$$

where n_p is the prism index, k_{SP} is the surface-plasmon wave vector, and ϵ_i is the dielectric constant of medium *i*. The last equality is approximate, because of the finite film

thickness. Solving for $\epsilon_1 \equiv \epsilon_{\text{Ag}}$ yields

$$\epsilon_1 = \epsilon_3 k_{\text{SP}}^2 / (\epsilon_3 \omega^2 / c^2 - k_{\text{SP}}^2). \quad (2)$$

Differentiating this equation with respect to k_{SP} yields the change in the resulting value of ϵ_1 produced by a small shift in k_{SP} :

$$\Delta\epsilon_1 = \frac{2k_{\text{SP}}\epsilon_3^2\omega^2c^2}{(\epsilon_3\omega^2/c^2 - k_{\text{SP}}^2)^2} \Delta k_{\text{SP}}. \quad (3)$$

In an earlier paper² I showed that the change in the surface-plasmon wave vector Δk_{SP} produced by a thin dielectric adlayer of thickness d_2 and dielectric constant ϵ_2 is given by

$$\Delta k_{\text{SP}} = \frac{k_{\text{SP}}^3 (\epsilon_2 - \epsilon_3)(\epsilon_1 - \epsilon_2)d_2}{\epsilon_2(\epsilon_1 k_1 + \epsilon_3 k_3)}, \quad (4)$$

where $k_i = (k_{\text{SP}}^2 - \epsilon_i \omega^2 / c^2)^{1/2}$. Substituting this result into Eq. (3) and simplifying gives an approximate expression for the error $\Delta\epsilon_1$ resulting from ignoring the adlayer in the

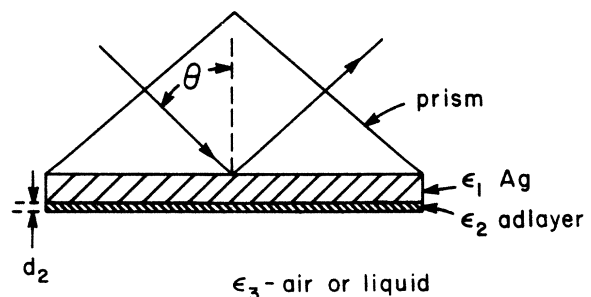


FIG. 1. Geometry for surface-plasmon-excitation ATR measurements.

original determination of ϵ_1 ,

$$\Delta\epsilon_1 = \frac{4\pi d_2(-\epsilon_1 - \epsilon_3)^{1/2}(\epsilon_2 - \epsilon_3)(\epsilon_1 - \epsilon_2)}{\epsilon_2\lambda(1 + \epsilon_3^2/\epsilon_1^2)} \quad (5)$$

This quantity is to be added to the measured ϵ_1 to correct it for the presence of the contaminating layer. Since $\Delta\epsilon_1$ is small, the measured ϵ_1 may be used on the right of Eq. (5). The correction will generally make a bigger shift in the air-interface result, since $\epsilon_2 - \epsilon_3$ will be larger; and since the shift is negative, it will tend to reduce the differences between the air- and liquid-interface results.

There are two adjustable parameters in Eq. (5), and, since Eq. (5) is only valid for fairly thick Ag films, I choose these to minimize the differences between the air- and liquid-interface values for the thicker-film data (58.4 nm) of Gugger *et al.* This yields $\epsilon_2 = 4$ and $d_2 = 12$ Å, with about a 30% uncertainty on each quantity. The results of correcting the 58.4-nm-film data in Ref. 1 with Eq. (5) and these parameters are summarized in Table I.

Figure 2 shows a comparison of $\text{Re}(\epsilon_{\text{Ag}})$ from Table I with data by Otter,³ obtained using ellipsometry, and by Eagen and Weber,⁴ obtained using the surface-plasmon resonance method. Both of these sets of measurements were done in ultrahigh vacuum (UHV) at the metal-vacuum interface. The solid straight line is a weighted least-squares fit to these *in situ* UHV points. (The lowest data point of Otter, at $\lambda = 0.66$ μm , has been omitted, since it has a much bigger uncertainty and falls well above the straight line.) Not shown, but also falling on the solid line in Fig. 2, are the substrate interface measurements of Weber and McCarthy⁵ and the film transmission and reflection data of Dujardin and Thèye.⁶ Note that the corrected values of Gugger *et al.*¹ not only agree with each other, but now also with data from several other experiments obtained with much cleaner surfaces. The ω_p values obtained from a Drude fit to the corrected data of Gugger *et al.* still show a slight, but much reduced, difference at the two interfaces. This difference could easily be accounted for by allowing some dispersion in the adlayer dielectric constant. Such a refinement to the present model does not appear warranted, however, in view of the fact that the adlayer, particularly its physisorbed com-

ponents, will undoubtedly be modified upon immersion in the liquid.

The parameters chosen for the contamination layer are reasonable. Oxygen is known to form a chemisorbed layer on a clean Ag surface;^{4,7,8} O'Handley, Burge, Jasperson, and Ashley⁷ estimate its thickness at 3 Å and $\epsilon = 5-10$. Upon exposure to room air there will be physisorbed O_2 and H_2O .^{4,7} The thickness of the physisorbed water layer has been estimated at 20 Å.⁷ In addition, Ag_2S ($\epsilon = 9$) will begin to form at the rate of 2 Å/day when the Ag surface is exposed.^{9,10} Since the contamination layer will probably have several components, the parameters used here ($\epsilon_2 = 4$ and $d_2 = 12$ Å) should only be considered as "effective" quantities describing the optical response of a rather inhomogeneous layer.

Gugger *et al.* also note systematic differences in $\text{Im}(\epsilon_{\text{Ag}})$ at the air and liquid interfaces. In 14 of 16 measurements on two films the apparent $\text{Im}(\epsilon_{\text{Ag}})$ is larger at the liquid interface. This trend is consistent with an absorbing adlayer as can be shown by using Eq. (5) to determine the first-order correction to $\text{Im}(\epsilon_{\text{Ag}})$. Estimating these corrections, however, which depend on the imaginary part of the adlayer dielectric constant and are apt to be even larger than those for $\text{Re}(\epsilon_{\text{Ag}})$, is not so easily done.

TABLE I. $\text{Re}(\epsilon_{\text{Ag}})$ from Gugger *et al.* (Ref. 1) at the air ($\epsilon_3 = 1$) and CCl_4 ($\epsilon_3 = 2.13$) interfaces for their 58.4-nm-thick film.

λ (μm)	Air ^a interface	Liquid ^a interface	Air ^b interface	Liquid ^b interface
0.4416	-6.32	-6.47	-6.92	-6.78
0.4880	-8.77	-9.09	-9.59	-9.56
0.5145	-10.27	-10.53	-11.21	-11.08
0.5309	-11.15	-11.49	-12.17	-12.09
0.5682	-13.37	-13.83	-14.58	-14.57
0.6328	-17.45	-17.94	-19.00	-18.90
0.6471	-18.58	-19.33	-20.23	-20.37
0.6764	-20.49	-21.45	-22.29	-22.60

^aOriginal data in Table I of Ref. 1.

^bOriginal data corrected using Eq. (5) with $\epsilon_2 = 4$ and $d_2 = 12$ Å.

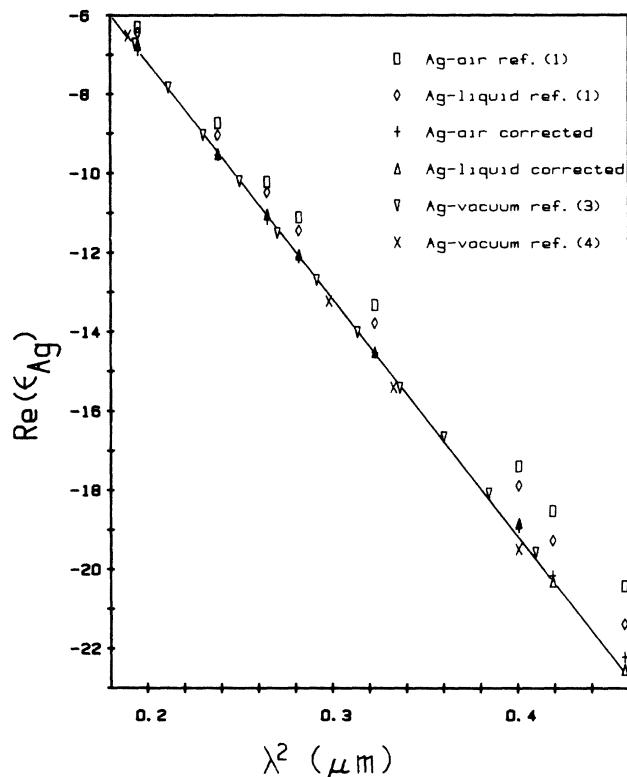


FIG. 2. The (\square) and (\diamond) points are the original data for the 58.4-nm film of Gugger *et al.*, appearing as the second and third columns in Table I. The ($+$) and (Δ) points, which overlap, are the corresponding corrected data appearing as the last two columns in Table I. The (∇) points are the ellipsometric data of Otter (Ref. 3), and the (\times) points are the surface-plasmon resonance data of Eagen and Weber (Ref. 4). The straight line is a weighted least-squares fit to the ∇ and \times points.

The finite metal-film thickness has a much bigger effect in the determination of $\text{Im}(\epsilon_{\text{Ag}})$; the differences in $\text{Im}(\epsilon)$ for the various components of the adlayer may be 1–2 orders of magnitude, rather than just a factor of 2; and there may be a stronger wavelength dependence to the absorption in the adlayer. In any case, the presence of the adlayer will cause the reported values to be too large. This indeed appears to be the case. The values of $\text{Im}(\epsilon_{\text{Ag}})$ in Table I of Gugger *et al.* are 50–100% larger than those measured in UHV (Refs. 3 and 4) or at the substrate interface.⁵ Since a large component of $\text{Im}(\epsilon_{\text{Ag}})$ is apparently coming from the contamination layer, which again will be modified somewhat upon immersion, there is no justification for attributing the resulting differences in this quantity to an index-of-refraction-induced effect in the Ag film.

To conclude, I believe the anomalous results of Gugger *et al.* are caused primarily by surface contamination on their Ag films. The question as to whether or not metal optical constants are changed by an adjacent dielectric is still an open one. It has been addressed previously by Eagen and Weber (see Table I of Ref. 4), albeit on different surfaces of different films. They found for Ag, Au, and Cu films measured at several wavelengths that, outside of the normal sample-to-sample variation, there were no systematic differences between the ϵ values obtained at the metal-vacuum and metal-fused-silica interfaces. However, the sample-to-sample variations were of the same magnitude as the differences found by Gugger *et al.*, so a small effect due to the adjacent dielectric could not be ruled out.

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