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Measurement of Roughness-Induced
Wavelength Corrections to the Surface
Plasmon Resonance in Silver

MASTER

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Abstract

A systematic study has been made of the wavelength position of the surface plasma resonance in roughened silver foils. Frequency shifts in the resonance peak, produced by varying surface roughness parameters, have been interpreted using a model calculation. A self-consistent comparison has been made to angular scattered-light distributions from the same foils. Remarks are given concerning changes in silver reflectivity due to annealing.

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Detailed shifts in the surface plasma resonance of a metal as a function of surface roughness conditions have not previously been examined experimentally. However, a number of calculations of roughness scattering¹⁻³ have suggested that such small effects can be used to advantage to study surface structure. With such a view we have carried out consistent reflectance and scattering measurements on a number of sets of roughened silver foils to examine how varying the roughness modifies their scattering properties.

To produce surfaces which could be examined, silver of $\sim 0.5 \mu\text{m}$ thickness was evaporated onto $0.05 \mu\text{m}$ to $0.3 \mu\text{m}$ thick calcium fluoride underlayers on glass substrates. Using this procedure we found that roughness scattering tended to increase monotonically with underlayer thickness. Evaporation of increasing amounts ($0.3 \mu\text{m}$ to $0.8 \mu\text{m}$) of silver on calcium fluoride did not lead to monotonic roughness growth. Further, annealing silver is believed to change its optical properties as well as its roughness. Surface corrugations were also induced by evaporating silver onto random dispersions of very small ($900 \text{ \AA}$) latex spheres.

In the work of the theoretical groups cited,¹⁻³ roughness at a metal-air boundary is shown to give rise to induced surface dipole moments at the metal interface which may either scatter light out of or into the metal. The Joule loss in the metal due to the extra scattering modes caused by the dipole reradiation leads to a resonant change in the absorptivity and thus to a change in the reflectance. This is the surface plasma wave absorptance. Define the metal dielectric function as $\epsilon = \epsilon_R + i\epsilon_I$. Then for normally incident unpolarized light this differential reflectance contribution is given by

$$\Delta R_{sp} = \epsilon_1 k_0 |\sqrt{\epsilon} - 1|^2 \sum_K |\zeta_K|^2 \left(\frac{|\gamma|^2 + K^2}{\text{Im} \gamma} \right) \frac{\alpha^2}{|\epsilon \alpha + \gamma|^2} \quad (1)$$

where $k_0 = \omega/c$, K is the two-dimensional scattering wavevector on the surface, $\gamma = (K^2 - \epsilon k_0^2)^{1/2}$, and $\alpha = (K^2 - k_0^2)^{1/2}$. The K -th Fourier component of the surface roughness is ζ_K where the surface topography function $\zeta(\bar{R}) = \sum_K \zeta_K e^{i\bar{K} \cdot \bar{R}}$ and where $\bar{R}$ is the two-dimensional surface position vector. The largest contribution to ΔR_{sp} occurs for $\epsilon \alpha + \gamma = 0$, that is for surface wavevectors K such that

$$K^2 = k_0^2 \text{Re} \left(\frac{\epsilon}{\epsilon + 1} \right). \quad (2)$$

We have compared p- and s-wave light-scattering distributions to calculated surface scattering cross sections to determine surface parameters under the assumption of Gaussian correlations such that $|\zeta_K|^2 = \pi \zeta_0^2 a^2 e^{-K^2 a^2/4}$. The rms height of surface irregularities is ζ_0 , and the correlation length characterizing their horizontal distribution is a . The roughness spectrum given assumes a stochastic surface with no preferred wavevector. We checked this assumption by determining the power spectrum $|\zeta_K|^2$ at several Ar⁺ and He-Ne wavelengths and, in fact, found it to be an adequate assumption for foils analyzed below, though not all foils. However, roughness, for which $a < \lambda$, must be distinguished from waviness, for which $a > \lambda$.⁵ It is found experimentally that a number of surfaces have admixtures of both components. However, surfaces which are strictly wavy have only weak surface plasmon absorption; thus it is the limit $a < \lambda$ which we emphasize here.

In Fig. 1 we show both scattered-light distributions and surface plasma resonance reflectance for a set of films having increasing calcium flouride thickness. The trend for the scattering distributions in the progression

of example cases A through C is for the rms roughness height ζ_0 ($40 \text{ \AA} \lesssim \zeta_0 \lesssim 55 \text{ \AA}$) to increase simultaneously with the correlation length $\underline{a}$ ($790 \text{ \AA} \lesssim \underline{a} \lesssim 820 \text{ \AA}$). As mentioned, it has been necessary to introduce a small wavy component correction to the surface irregularity to ensure a good comparison of theory to experiment. Under the assumption of Gaussian correlations, the Fourier spectrum of roughness falls off at approximately $K = 2/\underline{a}$. An examination⁶ of the reflectance change ΔR_{sp} (Eq. (1)) shows that these highest wavevectors dominate in yielding the observed structure at the resonance peak. Thus, using Eq. (2) and the cutoff wavevector given above, we may consistently determine the surface plasma resonance wavelength. The portion of this dispersion curve of interest to us is shown in Fig. 2 as determined from previously measured optical constants⁷ for silver. The bare, solid curve is found from Eq. (2) and the dashed curve shows the same dispersion relation with inclusion of numerically calculated self-energy corrections.⁸ The surface plasma resonance frequencies determined for cases A, B, and C in this instance are approximately 3540, 3550, and 3580 $\text{\AA}$ which concur favorably with the experimental values 3525, 3530, and 3560 $\text{\AA}$ respectively. Numerical calculations as shown in Fig. 1 yield a more realistic comparison, since calculations averaging over all surface wavevectors K do not utilize the approximate cutoff criterion stated above.

The inclusion of the second-order roughness-induced correction to the dispersion relation shifts the surface plasma resonance wavelength λ_{sp} by about +60 to 90 $\text{\AA}$ if approximately self-consistent parameters ζ_0 and $\underline{a}$ (50 to 60 $\text{\AA}$, 800 $\text{\AA}$) are used in the analysis. If we leave out this correction, then for the roughness parameters given, the predicted λ_{sp} is too small when compared to experimental measurements. As an example, in the cases B'

and B (Fig. 2) we would then obtain 3450 Å and 3550 Å respectively as compared to the experimental value 3530 Å. These numbers are taken to give evidence that self-energy corrections play a role in establishing the surface plasma resonance wavelength locations; however, in view of various approximations inherent to this determination, the agreement should be viewed presently as somewhat tentative.

Let us now consider some of the important limitations to the analysis of corrugated films. Both the experimental scattering spectra and the surface plasmon absorption contain details not accounted for in the lowest-order theories presently utilized. A strong discrepancy is that as the roughness perturbation increases, the experimental polarized p-wave scattering cross section remains higher than predicted for scattering angles between about 25° and 50° . Though not included in the present data analysis, we find that this difference can be reduced by including a contribution due to perturbed metal surface currents normal to the interface. Another limitation is the Gaussian roughness spectrum assumption. It is not assured that the same $|\zeta_K|^2$ spectrum applies to both metal and air scattering, since these distributions test different portions of surface scattering K-space. The tendency found was that the internal metal scattering required a slightly larger $|\zeta_K|^2$ than for air scattering. In other words, a tendency in the consistency analysis was to require larger roughness parameters ζ_0 (up to ~25%) in roughness absorption than in scattering. Furthermore, least squares comparisons of experimental data introduced the complication of multiple parameter pairs ζ_0 and $\underline{a}$ which yield best scattering data fits. Nonetheless $\zeta_0, \underline{a}$ values could be found to nearly consistently reproduce both scattering

and surface plasmon measurements. Finally, we believe that the trend established in cases A through C of Fig. 1 is probably more accurately verifiable than the absolute value of these roughness variables which may be established only to perhaps 5 to 10%.

We wish to include comments on annealing silver-on-calcium-fluoride films. The outcome of this experiment is contrary to expectation; namely that the surface plasmon peak is observed to shift to lower wavelength (Fig. 3). Annealing might be expected to average out the higher Fourier roughness components. As in our previous analysis this would result in a shift of the surface plasmon to longer wavelengths. For 15 to 30 minute anneals of fresh foils at 300°C in an inert argon atmosphere, an examination of the scattering distribution shows relatively small changes in the angular scattering, while changes seen would support interpretation of a surface plasmon shift to higher wavelength.

Consequently, we suggest that the annealing may change the optical constants slightly instead, particularly the electronic relaxation rate and thus ϵ_I . For simplicity we here assume that only ϵ_I changes and that the roughness spectrum of the surface is fixed. Hence, by considering the right-hand side of Eq. (2) as a function of ω and ϵ_I , and assuming $|\epsilon_R| \gg \epsilon_I$, we have

$$\frac{\delta\omega}{\omega} = \frac{-\delta(\epsilon_I^2)}{2(\epsilon_R+1) \left[\epsilon_R(\epsilon_R+1) + \frac{\omega}{2} \frac{d\epsilon_R}{d\omega} \right]}. \quad (3)$$

Using the measured resonance value of $\epsilon = -1.9 + 0.3i$, we obtain $\delta\omega/\omega = +0.07 \delta(\epsilon_I^2)$ which suggests $\delta\epsilon_I$ of 0.25 to 0.5 to yield measured shifts $\delta\omega/\omega$ of 0.01 to 0.02.

The observed crossing of reflectance curves near 5000 Å can also be understood from this assumption. From the normal-incidence reflectance coefficient (with $|\epsilon_R| \gg \epsilon_I$) we obtain $\delta R = -\gamma \delta \epsilon_I / \sqrt{|\epsilon_R|} (1 + |\epsilon_R|) = -0.04 \delta \epsilon_I$ at 5500 Å. Thus, the observed reflectance decrease at this wavelength of 0.01 to 0.02 could again be induced by changes $\delta \epsilon_I$ of approximately 0.25 to 0.5, consistent with the surface plasmon shift. Such changes may be caused by surface diffusion of any residual surface atoms into the metal, although a metallic structural change may be more important instead. Similar complications due to metal annealing have been observed for aluminum⁹ where the possible competition of metal surface crystallite configurations and roughness during relaxation suggest that the annealed metal film state is not simply one of minimum roughness.

The authors are very grateful to Ross Potoff for his excellent assistance in rough foil preparation. This work was supported by Department of Energy contract EG-77-S-02-4381.

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FIGURE CAPTIONS

Fig. 1. Scattered light distributions at $\lambda = 4579 \text{ \AA}$ and reflectance near the screened plasma edge for rough silver foils of increasing roughness (A-C). Roughness parameters (ζ_0, a) give best fits (dashed lines) to angular scattering data (points). To improve agreement at low scattering angle, parameters (ζ_0', a') of a wavy surface component have been included. The reflectance calculations make use of the parameters obtained from scattering.

Fig. 2. Surface plasmon dispersion curve plotted from Eq. (2) showing the surface wavevector K versus the surface plasmon frequency ω (solid line). The displaced curve (dashed line) shows the result of a numerical calculation of a second-order scattering correction to the dispersion relation (following Ref. 8). The points A through C on the displaced curve indicate the ΔR_{sp} peak positions obtained from the approximate criterion that roughness components having $K = 2/a$ dominate in determining the resonance frequency. Roughness values $\zeta_0 = 60 \text{ \AA}$ and $a = 800 \text{ \AA}$ on the renormalized, dashed curve show nearly self-consistent parameters obtained in order to locate the calculated surface plasma resonance at a wavelength in approximate agreement with experiment.

Fig. 3. Reflectivity versus wavelength for a fresh, rough silver foil (F) compared to the same foil annealed (A) for approximately a half hour at 300°C in an inert atmosphere of argon. The surface plasma resonance is observed to shift to higher energy with annealing while decreasing slightly in amplitude.