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Measurement of the correlation between the specular reflectance and surface roughness of Ag films

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We present here an empirical relationship between the root-mean-square surface roughness and the loss in specular reflectance at the wavelength of 3500 Å for silver films having surface roughness between 5 and 35 Å. Films deposited on super-smooth substrates and films whose roughness was purposely enhanced were used for these measurements. From these data and the Elson-Ritchie theory the correlation lengths for our films were determined.

I. INTRODUCTION

Our purpose of this paper is to present quantitative measurements of the correlation between the near-normal specular reflectance of Ag films and the root-mean-square (rms) roughness of the film. The method we used to measure the rms roughness was the interferometric method of observation of the fringes of equal chromatic order, the FECO method.[1-3]

There are two optical methods for measuring the rms surface roughness of metal films: (i) The FECO method that we used for our work and which is thoroughly discussed in Refs. 1–3. (ii) The diffuse reflectance method where the intensity of the diffusely scattered radiation is measured and then compared to that predicted by a suitable theory. The theoretical description usually contains two adjustable parameters (δ, the rms roughness and σ, the correlation length) which allow a fit to be obtained. This method is less direct than the former but has been used by many workers.[4-11] These previously published reports cover the range of about 5 Å to several thousand angstroms for the rms roughness. However, the experimental situation is such that for the very smooth films the value obtained for δ depends very much on the extrapolation of the roughness for $k \to 0$, where k is the wave number associated with the surface.[7]

Because of this uncertainty in the extrapolation and the dependence of the diffuse reflectance method on theoretical prescriptions, we chose to measure the change in the near-normal specular reflectance at the wavelength 3500 Å, the surface-plasmon wavelength of Ag, as the roughness of the films was varied. Since the rms roughness was determined by the FECO method, the roughness and reflectance measurements are independent and thus should remove any annoying dependency of their relationship on assumptions concerning the autocorrelation function and correlation length of the surface.

II. EXPERIMENTAL

The spirit of our effort was to obtain the most accurate measurements possible and care was taken to ensure the quality of the Ag samples and the accuracy of the optical measurements. The following discussion considers the quartz substrates and their cleaning, the metal deposition techniques, the reflectance measurements, and the FECO measurements.

The substrates used for both the samples and reference films were fused quartz discs which had been bowl-feed polished in excess of 40 h.[12] Such polishing has been reported to produce surfaces with an rms roughness of about 3 Å.[5] The Ag samples were deposited on 32.0-mm diameter discs while the Ag references were deposited on 12.5-mm diameter discs. The difference in diameter of the two substrates eliminated the problem of nonparallelism of the two surfaces when they were brought into contact in the FECO measurements.

All substrates were first hand cleaned with a commercial glass cleaner and cleaned a second time in an ultrasonic cleaner containing a dilute solution of glass cleaner. The substrates were then rinsed in an ultrasonic cleaner which had freshly deionized water constantly being pumped into the tank. The conductivity of the rinse water was monitored and the rinse cycle stopped when the conductivity reached its initial value. After the rinse the substrates were allowed to air dry in a dust-free chamber and then placed immediately in the vacuum chamber.

Two types of Ag samples were prepared for this study: (1) Thick films (1500 Å) deposited on the super-smooth substrates as a single layer. These films exhibited rms roughness of between 5 and 10 Å. This roughness evidently arises because of residual substrate roughness and the deposition process. (2) Thick films deposited as two separate layers on the super-smooth substrates. The first

layer was approximately half of the intended final thickness of 1500 Å and was heated to roughen the surface. The second layer was deposited later to bring the total thickness to 1500 Å.

All of the Ag layers were prepared by evaporating 99.9999% pure Ag pellets in an ion-pumped vacuum chamber at a pressure of 10^{-8} Torr. The thickness of all films was determined by a quartz crystal thickness monitor. An electronic shutter was used to control the thickness of each film and to insure that no residual contaminants in the silver or on the resistance heated boat reached the substrate upon initial heating.

Type-2 samples were prepared by depositing 750 Å of Ag onto the substrates and then heating the samples in air for different times and at different temperatures to give various degrees of agglomeration. An additional 750-Å thickness of Ag was then deposited over the first layer to insure the same chemical composition of the surfaces for both types of samples.

The reference surfaces were prepared by depositing 400 Å of Ag onto one of the smaller substrates. The thickness of 400 Å was chosen so that the reference surface had a reflectance of about 95% at a wavelength of 5500 Å. When not in use the reference and sample films were stored in a nitrogen atmosphere to protect them from tarnish. It was found that Ag films could be stored for up to one month in the nitrogen atmosphere without visible deterioration of the surface. All samples used in this study were used within hours after their preparation. The reference surfaces needed to be remade after using them for about three samples since the repeated contact destroyed portions of the surface.

The near-normal specular reflectance of the surfaces was measured in air from 2700 Å to a wavelength of 5000 Å with the aid of a McPherson 216 scanning monochromator. The incident and singly reflected intensities at the various wavelengths were detected by a photomultiplier tube whose output was recorded on a continuous drive chart recorder. The reflectance was measured at an incidence angle of 7° and the light intensity could be determined to within ± 0.5%. Each sample had its reflectance measurements begun within 15 min after being removed from the vacuum chamber and at least two reflectance measurements were taken of each sample to check the precision.

Each film surface was examined with the FECO interferometer. For maximum accuracy we found it necessary to calibrate the wavelength drive mechanism of the Hilger-Watts grating spectrometer used in the FECO. The micrometer drive positions of the grating drive were recorded at the wavelengths of the spectral lines of mercury and sodium lamps. A linear least-squares fit to the micrometer readings versus these wavelengths was then made. Because of deviations from this linear line it was necessary to add a correction term to the wavelength determined from the least-squares equation. With these considerations it was possible to obtain a wavelength accuracy of ± 1.0 Å with the spectrometer.

The actual determination of the film roughness consisted of first aligning the FECO plates such that the fringes were parallel to the eyepiece hairline and only three or four fringes were present in the visible wavelengths. The fringe spacing and fringe width were then measured a minimum of three times for each sample. The accuracy of the FECO measurements is limited by the ability of the eye to define the edge of the fringes; thus the accuracy improves with the width of the fringe.

III. RESULTS AND DISCUSSION

This section presents the two main results of this study. The first is the experimentally derived relationship between the specular reflectance at $\lambda = 3500$ Å and the rms roughness for Ag films. The second is the calculation of the correlation length as a function of the rms roughness.

Figure 1 shows the specular reflectance of two of the 20 samples prepared for this study together with the measured reflectance of a super-smooth Ag film.[13] The dip in reflectance near $\lambda = 3500$ Å for curves *B* and *C* is caused by the absorption of light from the specular beam by the excitation of surface plasmons on the rough surface. Curve *A* does not exhibit this reflectance minimum since

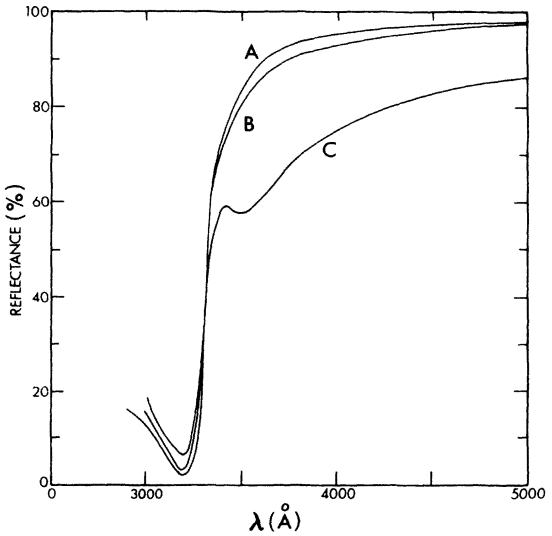

FIG. 1. Specular reflectance of Ag films with increasing surface roughness. Curve *A* is smooth Ag from Ref. 13 while curves *B* and *C* are from samples prepared for this work.

this film is smooth to the degree that surface-plasmon excitation is negligible. The difference in the reflectance near 3500 Å between the super-smooth film and any other film is then a measure of the rms roughness of that film's surface. We will not show the individual reflectance scans for each of the twenty films but instead show the difference in reflectance at $\lambda = 3500$ Å, ΔR, between the sample films and the super-smooth film. It should be emphasized that the super-smooth reflectance curve used as our standard is that reported in Ref. 13 and was identical to the reflectance of a few Ag films prepared in our laboratory. We found that these super-smooth films seemed to just happen rather than occur because of any special techniques used during the deposition process. Starting with a super-smooth substrate does not ensure obtaining a super-smooth film every time.

Each of the Ag samples prepared during this study had its rms roughness determined by FECO interferometry. The Ag sample and a Ag reference were mounted parallel and close together and then illuminated normally with white light. The ensuing destructive interference fringes were separated according to wavelength by imaging them onto the slit of the spectrometer. Roughness of the sample is then represented by the displacements of the fringe center in the eyepiece.

The optical path length, $L_{\text{O.P.}}$, between the two surfaces for destructive interference to occur is

$$L_{\text{O.P.}} = nd + \lambda\beta/2\pi = \tfrac{1}{2}(N+1)\lambda, \tag{1}$$

where β is π minus the phase change on reflection from silver, N is the order of interference, n is the index of refraction of the gap material, and d is the geometrical separation of the two reflective surfaces. The quantity $\lambda\beta/2\pi$ is nearly independent of wavelength and is thus regarded as a constant. The peak-to-peak surface roughness δ_{pp} is then related to the width of the fringe by

$$\delta_{pp} = \tfrac{1}{2}[\Delta N\lambda'/(\lambda - \lambda')]\Delta\lambda\,, \tag{2}$$

where ΔN is the difference in orders of interference for the fringes, $\Delta\lambda$ is the width of the fringe, λ is the wavelength where the fringe is located, and λ' is the wavelength of the shorter wavelength adjacent fringe if $\Delta N = 1$. In this study ΔN was always taken to be equal to one.

If the roughness is assumed to have a Gaussian height distribution then the rms roughness is related to the value of δ_{pp} by

$$\delta = \delta_{pp}/2\sqrt{2}\,. \tag{3}$$

The values of δ that we report here are calculated from Eqs. (2) and (3), thus the tacit assumption of a Gaussian roughness distribution is included.

The δ obtained from Eq. (3) is composed of contributions from the reference surface as well as the sample surface. The contribution of the reference surface was determined by using two reference substrates as the FECO interferometer plates and assuming each surface contributed equally to the measured fringe width. The rms roughness of each surface is then the rms value from Eq. (3) divided by $\sqrt{2}$. Our reference surfaces consistently indicated values of 7 Å or less for their rms roughness. We believe that 7 Å is a conservative figure since the first Ag film must be thin enough to allow some light to pass to the second surface in order to establish the interference pattern. This thinner film has a lower reflectance than the opaque second surface and thus serves to broaden the fringe width.

Figure 2 shows our experimental results for those samples of type 2 which had their roughness enhanced. The reflectance of these samples was corrected for loss of intensity due to diffuse scattering of the incident beam.[6] The effect of the largest correction for this scattering amounted to a lowering of about 0.5% of ΔR for the roughest sample. The ΔR values shown are thus representative of surface-plasmon effects only.

Included in this figure are the results of Stanford *et al.*[13] from their diffuse reflectance measurements on Ag films which had their roughness enhanced by depositing the Ag onto CaF_2. From

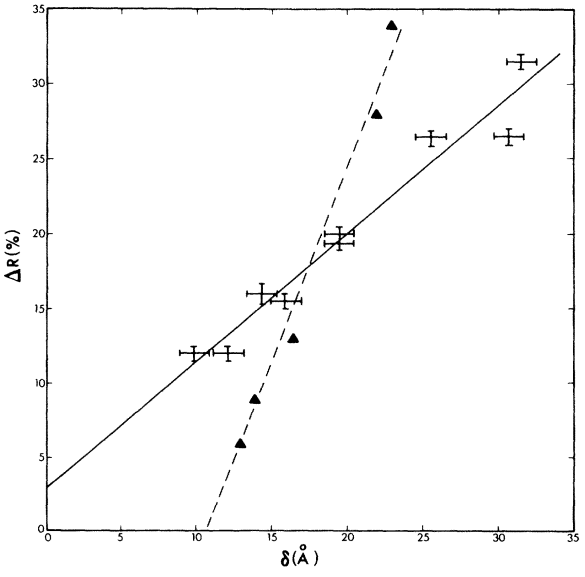

FIG. 2. Experimentally observed reflectance drops in roughened Ag films as a function of the surface roughness δ as measured with FECO interferometer. The points with error bars are results of the present work whereas the solid triangles are taken from the data of Ref. 13. The straight lines are least-squares fits to the experimental points.

their measurements of ΔR and with the aid of a scalar scattering theory they determined δ as a function of ΔR. A linear least-squares fit to our data and their data indicates the wide variance of the extrapolated value of δ at $\Delta R = 0$. The differences between the two sets of data are unknown but their determination of δ is dependent on the roughness correlation length σ. Both δ and σ affect the measured ΔR and usually σ and δ are not known *a priori*. This is one of the uncertainties connected with this method of determining the roughness parameters from a measurement of ΔR alone. Our data, since ΔR and δ are determined independently, not only allow ΔR vs δ but also σ to be determined if an appropriate autocorrelation function for the roughness spectrum is chosen.

When one now considers the results from our experiments on type-1 films the correlation between ΔR and δ is even more striking. Figure 3 shows a plot of the reflectance drop at 3500 Å versus the rms roughness of all samples prepared for this study. The solid line is a least-squares fit to the data and extrapolation to $\Delta R = 0$ indicates that $\delta \simeq 0$ also. This is a physically satisfying conclusion since one expects no plasmon absorption on a planar surface. The experimental points in Fig. 3 have been corrected for the residual roughness of the reference surface. This correction is important for the smoother films but of negligible importance for the rougher films.

After the experimental relationship between ΔR and δ is known a calculation of σ can be made from the theory of Elson and Ritchie.[14] We assume a Gaussian autocorrelation function for illustrative purposes. A plot of our measured values of δ and the corresponding calculated values of σ are shown in Fig. 4 together with the δ and σ values reported in Ref. 9. The most apparent feature of these data is the inverse behavior of σ with δ. Previous to Endriz and Spicer's data most workers believed that σ increased with δ because of physical arguments and the observation that the reflectance minima shifts to longer wavelengths as δ increases. This is what is predicted by mathematical models of rough surfaces. It has now been shown that the surface plasmon travels with a lower phase velocity on a rough film than on a smooth film and this accounts for the shift in the reflective minima.[15] The slowing of the plasmon is brought about by the rough air-metal interface acting as a boundary with an "effective" dielectric constant greater than a smooth air-metal interface. In addition, a recent paper by Braundmeier and Hall[16] presented evidence based on surface-plasmon radiation patterns which implied that the correlation length of a surface may increase without a corresponding increase in the rms roughness. The data of Fig. 4 support, we believe, the conclusion of Endriz and Spicer[9] that the correlation length bears an inverse relationship to the rms roughness.

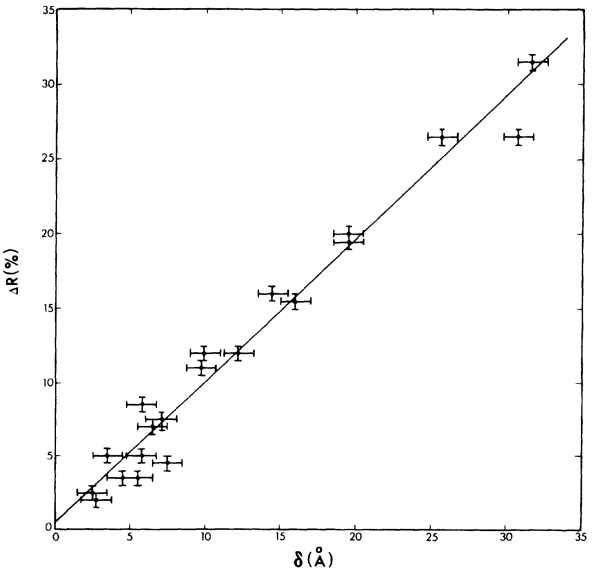

FIG. 3. Experimentally observed reflectance lossers at 3500 Å versus the rms roughness for both type-1 and type-2 samples. The solid line is a least-squares fit to the experimental data and has the equation $\Delta R = 0.415 + 0.961\delta$.

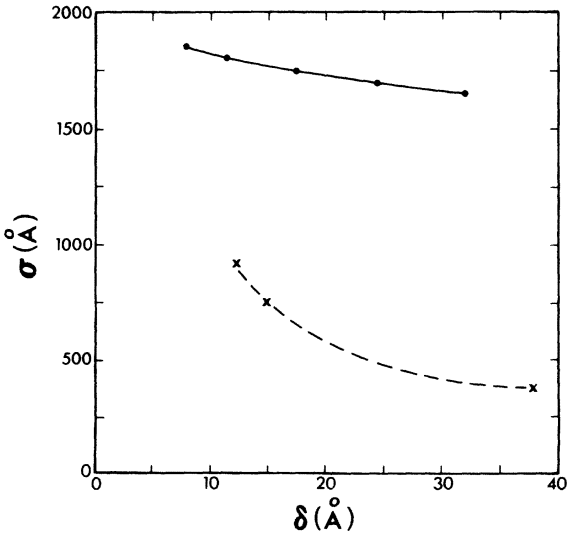

FIG. 4. Plot of the correlation length σ versus the rms roughness δ. The solid circles are the present work calculated from the data in Fig. 3 together with Elson and Ritchie's theory (Ref. 14) and assuming the roughness is describable by a Gaussian autocorrelation function. The dashed line is as smooth fit to the data of Endriz and Spicer (Ref. 9).

IV. CONCLUSIONS

Independent measurements of the rms roughness and the near-normal specular reflectance have been made on Ag films. These measurements showed a linear relation to exist between the magnitude of the reflectance minimum at $\lambda = 3500$ Å and the rms roughness of the various samples. From these data the correlation length was calculated from the Elson-Ritchie[14] theory with a Gaussian autocorrelation being assumed. It was found that the correlation length and the rms roughness are inversely proportional to one another.

The most useful aspect of the optical studies reported in this paper is the relationship between ΔR and δ. One can regard Fig. 3 as a calibration curve for the reflectance drops at $\lambda = 3500$ Å for Ag films in terms of the rms roughness of the film. This provides the experimentalist with a convenient aid in determining δ for his samples. For samples of materials other than Ag one can overcoat the surface with an opaque Ag layer and use the ΔR vs δ curve.

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