Au $4f$ levels, but no analysis of these is presented.

[18]The s and p core electrons of the same principal quantum number n as the valence d electrons should exhibit chemical shifts different from those of smaller n value. The latter lie inside the potential plateaus (Fig. 1) of both the valence d and conduction electrons, whereas the former overlap the shoulder of the d potential. Unfortunately, the $5s$ line of Au and the $4p$ line of Ag, which were examined experimentally in the Au-Ag system, were so broad that no meaningful shift differences, relative to the $4f$ and $3d$, were observable.

[19]See e.g., J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960).

[20]R. E. Watson, H. Ehrenreich, and L. Hodges, Phys. Rev. Letters 24, 829 (1970); and unpublished; R. E. Watson and H. Ehrenreich, Comments Solid State Phys. III, 109 (1970).

[21]We have employed in the F^0 integrations nonrelativistic free-atom Hartree-Fock or Hartree-Fock-Slater wave functions, normalized to the appropriate atomic volumes.

[22]See, e.g., D. E. Eastman, Phys. Rev. B 1, 1 (1970), where work functions are reported.

[23]L. Brewer, Science 161, 115 (1968).

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Study of Aluminum Films. I. Optical Studies of Reflectance Drops and Surface Oscillations on Controlled-Roughness Films*

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Ultrahigh-vacuum near-normal-incidence ultraviolet reflectance measurements on aluminum films of known rms surface roughness have confirmed recent theories of roughness-aided coupling to surface plasmons in free-electron-like metals and of roughness-induced light scattering. The notable success of these theories allowed the separation of experimentally observed reflectance drops into surface-plasmon-induced and scattered-light-induced components. These confirmed theories were combined with reflectance measurements to yield the surface-roughness spectra of the films studied over a spatial-frequency (wave-number) range of $\leq 1.4\times10^{-2}$ Å^{-1}. This is believed to be the first example of the use of both surface-plasmon-induced and scattered-light-induced reflectance effects for the determination of the surface-roughness spectra.

I. INTRODUCTION

Considerable theoretical[1-3] and experimental interest has developed concerning the optical[4,5] and photoemission[6] properties of roughened metallic surfaces. Optical studies have emphasized the measurement of surface-plasmon effects on rough surfaces, somewhat to the exclusion of equally significant and less understood roughness-induced scattered-light effects. Early studies by Jasperson and Schnatterly[4] confirmed the roughness-dependent coupling to surface plasmons in silver, and Stanford, Bennett, Bennett, Ashley, and Arakawa[4] showed this coupling on films of known (measured) rms surface-height variations. More recent studies by Feuerbacher and Steinman[5] substantiated the importance of roughness-aided coupling to surface plasmons in the nearly free-electron-like metal aluminum, but, unfortunately, no attempt was made to estimate the roughness of the Al films.

Preliminary roughness-dependent photoyield effects were first reported by Endriz and Spicer who attempted to describe them as resulting from the volume photoemission effect associated with the decay of surface plasmons. Here and in the succeeding paper[7] (referred to as Paper II) we report on current optical and photoemission studies of ultrahigh-vacuum-evaporated Al films of known rms roughness, which were designed to present a more definitive description of the processes involved. In analyzing these photoemission effects, it was found that the interpretation relied strongly upon a thorough understanding of roughness-dependent optical effects, particularly the less well understood scattered-light effects. Although optical effects of surface-plasmon coupling have been extensively studied, only the recent theoretical developments of Hunderi and Beaglehole,[8] Berreman,[9] and Ritchie[10] have furthered the understanding of scattered-light effects.

Because most of the existing theory of roughness-aided coupling to surface plasmons is applicable to nearly free-electron metals such as Al, it was believed that the roughness-dependent studies reported in this paper would provide confirmation of scattered-light theories and also the first opportunity to compare near-normal-incidence reflectance measurements of known roughness films to theories of surface-plasmon excitation. The investigation of Al also allows the examination of the importance of surface roughness in ultraviolet reflectance studies of polyvalent nearly free-electron metals.

Previous Al reflectance measurements have noted the sharp sensitivity of uv properties to preparation techniques; it has long been known, for example, that the uv reflectance of Al is extremely sensitive to surface preparation. In the past, however, observed drops in this reflectance have been attributed to contamination.[11–14] Our current experiments on controlled-roughness Al films were carried out in the ultrahigh vacuum; thus, any variations in reflectance must arise from inhomogeneities in the surface or film volume rather than from surface contamination.

The results discussed in this paper stress the agreement between the near-normal angle-of-incidence reflectance measurements and the surface-plasmon coupling theory of Elson and Ritchie; they also emphasize the apparent superiority of the Ritchie light-scattering theory to the previous "scalar" scattering theory. It is found that, in addition to providing improved understanding of the relative importance of surface-plasmon coupling and light scattering, these theories can be combined with experimental results to yield a great deal of information concerning the surface-roughness spectra.

II. THEORY OF ROUGHNESS-INDUCED OPTICAL EFFECTS IN NEARLY-FREE ELECTRON METALS

The theories discussed in this section are concerned primarily with roughness-aided coupling to surface plasmons and the roughness-induced diffuse scattering of incident light. A third process, roughness-induced anomalous light absorption as suggested by Beaglehole,[8,15] is discussed but not extensively pursued because a general theory has not been developed and the experimental results found in Paper II cast some doubt on the importance of this process.

A. Roughness-Aided Coupling to Surface Plasmons

The dispersion relationship for evanescence electromagnetic (em) waves (surface plasmons) propagating along the surface of a free-electron metal was first derived by Fano[16] and is given by

$$\omega_k^2 = \tfrac{1}{2}\omega_p^2 + c^2k^2 - (\tfrac{1}{4}\omega_p^4 + c^4k^4)^{1/2}, \qquad (1)$$

where ω_p is the volume plasma frequency for the free-electron metal and k is the wave number (directed parallel to the surface) of the surface plasmon.

A plot of ω_k vs k for a free-electron gas having the same volume plasma frequency as the experimentally observed value for Al ($\hbar\omega_p = 14.9$ eV) is shown in Fig. 1. Also shown is the dispersion relationship for a pure em wave propagating parallel to the metallic surface. Because the surface-plasmon dispersion curve never crosses the dispersion curve of an em wave incident at an arbitrary angle on the metal, the surface plasmon cannot couple to these photon modes and, as a result, cannot radiate into these modes or be excited by photons incident on a perfectly planar surface of the metal. For this reason, the surface-plasma oscillations (described in Fig. 1 and discussed throughout the remainder of this paper) are called nonradiative surface plasmons. This is to distinguish them from so-called radiative surface plasmons that can exist at certain frequencies in metallic films whose thicknesses are small compared to their optical penetration depths. These nonradiative surface plasmons and the external photon fields should be considered as orthogonalized modes of the same coupled em-field–electron-gas system.

Two significant modifications of the above expression for surface oscillations have been made. Ritchie and Wilems[1] and Crowell and Ritchie[2] have included the effects of a finite hydrodynamic speed

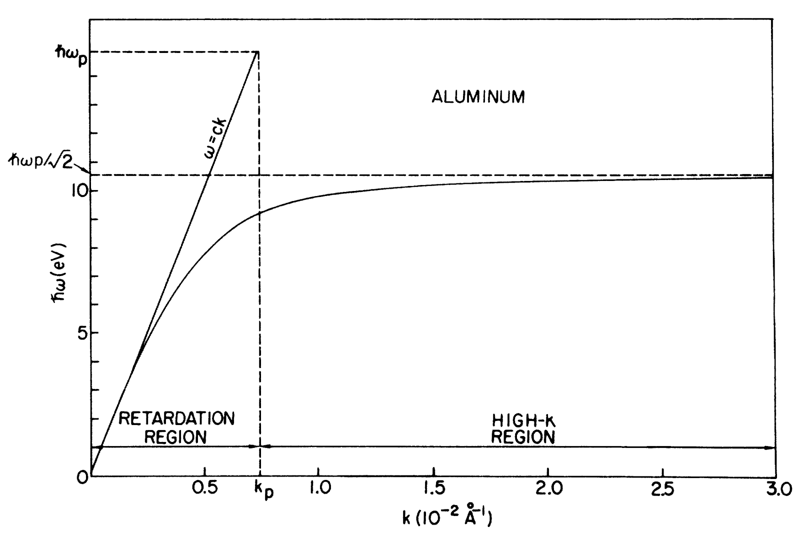

FIG. 1. Surface-plasmon dispersion curve for a free-electron metal having a plasma frequency ω_p equal to the experimentally determined plasma frequency of Al.

of propagation in an electron gas to yield a so-called hydrodynamic dispersion of the surface plasmons for high-k oscillations. Because the effects of this dispersion have not been observed clearly (either in the present or in previous optical studies), we will not be concerned with the details. In the second modification, Elson and Ritchie[3] included the effects of the lifetime broadening of surface oscillations in a real metal. These effects are important in interpreting the Al reflectance measurements described in this paper and the photoyield measurements described in Paper II. The details of their theory appear in the discussion that follows.

Stern[17,18] first pointed out that the inability to optically excite surface plasmons could be frustrated by allowing surface roughness to conserve momentum tangential to the surface. The first quantitative analysis of such coupling (essentially coupling to high-k plasmons) was carried out by Ritchie and Wilems.[1] Crowell and Ritchie[2] extended this theory to include coupling to the lower plasmons that lie in what Fig. 1 refers to as the retardation region. Recent experiments[4] have indicated that, for real surfaces, coupling to plasmons lying in this low-k region is strongest.

Elson and Ritchie[3] have since derived an alternate expression for roughness-aided coupling to plasmons in the retardation region. Their theory employs what is believed to be a superior perturbation technique and allows for the inclusion of lifetime effects rising in real metals having finite $\epsilon_2(\hbar\omega)$. The probability that a normally incident photon of energy $\hbar\omega$ will excite a surface plasmon can be expressed as a reflectance drop as

$$\Delta R_{sp}(\hbar\omega)=\frac{\sigma^2\omega^4}{c^4}\,\frac{\epsilon_1^2}{(\epsilon_1^2-1)^2[-(\epsilon_1+1)]^{1/2}}\left\{3(\epsilon_1-1)+\omega\,\frac{d\epsilon_1}{d\omega}\left[1-\left(\frac{\epsilon_1+1}{\epsilon_1}\right)^{1/2}\right]\right\}^2 g\left[\frac{\omega}{c}\left(\frac{\epsilon_1}{\epsilon_1+1}\right)^{1/2}\right], \tag{2}$$

where $\sigma^2 g\{k=(\omega/c)[\epsilon_1/(\epsilon_1+1)^{1/2}]\}$ is the Fourier transform of the surface-height-variation autocorrelation function, σ is the rms surface-height variation, and $\epsilon_1(\hbar\omega)$ is the real part of the dielectric constant of the metal. If $\epsilon_1 \gg \epsilon_2$ (marginally applicable in Al) is assumed, then Elson and Ritchie have shown that the above expression can be modified to include plasmon-lifetime broadening effects. In these circumstances we have the reflectance drop,

$$\Delta R_{sp}(\hbar\omega)=\frac{\sigma^2\omega^3}{2\pi c^2}\int_0^\infty \frac{1}{1-\epsilon_1}\left\{3(\epsilon_1-1)+\omega_k\frac{d\epsilon_1}{d\omega}\left[1-\left(\frac{\epsilon_1+1}{\epsilon_1}\right)^{1/2}\right]\right\}^2 \frac{k}{P_k}\,\frac{\gamma_k}{(\omega-\omega_k)^2+(\frac{1}{2}\gamma_k)^2}\,g(k)\,dk. \tag{3}$$

The function of ϵ_1 inside the integral is evaluated at $\omega=\omega_k$, ω_k is the solution to

$$k^2=\frac{\omega_k^2}{c^2}\,\frac{\epsilon_1(\omega_k)}{1+\epsilon_1(\omega_k)}\ ,$$

where k is the wave number characterizing a given surface oscillation, ω_k is its characteristic frequency, and $\gamma_k=2\epsilon_2(\omega_k)/(d\epsilon_1/d\omega)$ is its characteristic linewidth. In the above integral, P_k is given by

$$(1-\epsilon_1)\,[-(1+\epsilon_1)]^{1/2}\,\epsilon_1^{-2}\left[\epsilon_1(\epsilon_1+1)+\tfrac{1}{2}\omega\,\frac{d\epsilon_1}{d\omega}\right]\ .$$

This expression simply characterizes the surface-plasmon-induced reflectance drop on a rough surface in terms of an arbitrary transform of the autocorrelation function of the surface and of the optical constants of the metal.

B. Roughness-Induced Reflectance Drops Exclusive of Surface-Plasmon Coupling

Because an exact solution to the Maxwell equations for a light beam normally incident on an arbitrary rough surface is not possible, an exact solution for the drop in reflectance associated with anomalous absorption or scattering of the incident beam cannot be obtained; however, approximate theories have been developed. We have described one theory of anomalous energy absorption associated with an excitation of surface waves on a slightly roughened surface. Further attempts to explain this phenomenon can be divided into theories that express both the absorbed and scattered light in terms of specific surface-roughness models and theories that treat only scattered light but derive such scattered light in terms of a general surface-roughness model.

Twersky,[19] Berreman,[9] and Hunderi and Beaglehole[8] have developed approaches to the anomalous absorption and scattering of light from surfaces characterized by spherical and hemispherical surface inhomogeneities; these are applicable to materials having arbitrary optical constants. Although these approaches were highly restrictive in their choice of a surface-roughness model, they did predict that the scattered-light components in such exact solutions varied from those predicted in the "scalar" scattering theory (see below) and that the anomalous absorbed light resulting from processes other than surface-plasmon excitation could be significant in the excitations of metals in which ϵ_2 was appreciable.

The real rough surfaces are not well approximated by hemispherical or spherical bumps and, unfortunately, the above theories are sensitive to the surface model used. The first attempt to calculate scattered light in terms of a more general surface-roughness model was the Bennett-Porteus[20] "scalar" scattering approach based on the earlier theory of Davies.[21] This theory is applicable in the limit $|\epsilon_1| \gg 1$ and for arbitrary surface-roughness models whose characteristic height variations occur over distances parallel to the surface comparable to one wavelength. The distribution of surface heights is assumed Gaussian about the mean, and the autocorrelation function is assumed Gaussian with standard deviation $\bar{a}$ (comparable to λ), thus yielding for specularly reflected light from a material whose smooth surface reflectance is R_0,

$$R_s = R_0\, e^{-(4\pi\sigma)^2/\lambda^2}\,, \tag{4}$$

where σ is the rms height variation. One significant point is that the total fraction of light scattered out of the incident beam $\Delta R = R_0[1 - \exp - (4\pi\sigma)^2/\lambda^2]$ is totally independent of the autocorrelation length $\bar{a}$ and depends only on the light frequency and the rms height variation σ.

Recently, Elson and Ritchie[10] proposed a more general theory of scattered light applicable at all frequencies for which $\mathrm{Im}(\epsilon)$ is negligible. This approach obtained both the s-polarized ($\vec{E}$ field of the scattered photon is polarized perpendicular to the plane of emission) and the p-polarized ($\vec{E}$ field is parallel) scattered photons, as a function of the spectrum $\sigma^2 g(k)$ of a generalized surface-height-variation autocorrelation function for the special case of a free-electron metal. The differential probability of finding an s-polarized photon in the direction specified by the polar angle θ measured with respect to the surface normal and an azimuthal angle ϕ measured from the plane containing the surface normal and the $\vec{E}$ vector of the incident photon is

$$\frac{dP^{(S)}}{d\Omega} = \frac{\sigma^2\omega^4}{\pi^2 c^4} \sin^2\phi \cos^2\theta\, g\left(\frac{\omega \sin\theta}{c}\right). \tag{5}$$

For p-polarized photon scattering,

$$\frac{dP^{(P)}}{d\Omega} = \frac{\sigma^2\omega^4}{\pi^2 c^4} \cos^2\phi \cos^2\theta \frac{\sin^2\theta - \epsilon}{\sin^2\theta - \epsilon\cos^2\theta} \times \left(1 + \frac{2(-\epsilon)^{1/2}}{(\sin^2\theta - \epsilon)^{1/2}}\right)^2 g\left(\frac{\omega\sin\theta}{c}\right). \tag{6}$$

An extremely important difference between this and the "scalar" theory is that the above approach implies that the total scattered light at a given frequency is strongly dependent on the shape of the surface-roughness spectrum, as well as on its integral σ^2. The Elson-Ritchie theories of roughness-aided light scattering and of roughness-aided coupling to surface plasmons lend themselves to a single unified interpretation. For a surface characterized by an autocorrelation function whose spectrum is given by $\sigma^2 g(k)$, the momentum-conserving transitions are possible from an initial incident photon to a final scattered photon emitted at polar angle θ and having momentum $k = (\omega \sin\theta)/c$ parallel to the surface. The ability of the surface to provide such momentum conservation is proportional to $g[(\omega\sin\theta)/c]$; thus, only those surface-roughness components less than ω/c are actually involved in scattering light, and those spectral components above ω/c allow excitation of the surface plasmons. As a result, it is apparent that, for a given rms roughness σ, a trade off occurs between light scattered by the roughened surface and light absorbed by plasmons. For large correlation lengths, the normalized roughness spectrum $g(k)$ will be concentrated at small k, and, therefore, a large fraction of the spectrum will be concentrated in a spectral region for which $k < \omega/c$ and the bulk of these roughness components will be able to partake in the scattering of light. The value of $g(k)$ for $k > \omega/c$ momenta (which allows coupling to plasmons) will be correspondingly small. For short correlation lengths, $g(k)$ will extend to higher k values, light scattering will be lower, and coupling to surface plasmons will be correspondingly higher.

Figure 2 is a theoretical plot of the Al reflectance that one would expect from an Al film characterized by a surface having a Gaussian autocorrelation function with a rms height variation of 15 Å and a correlation length of 450 Å; the dashed line is the expected reflectance if only scattered-light effects were included. Also shown is the expected reflectance drop, assuming the "scalar" theory of scattered light. Figure 3 is a plot of the scattered-light

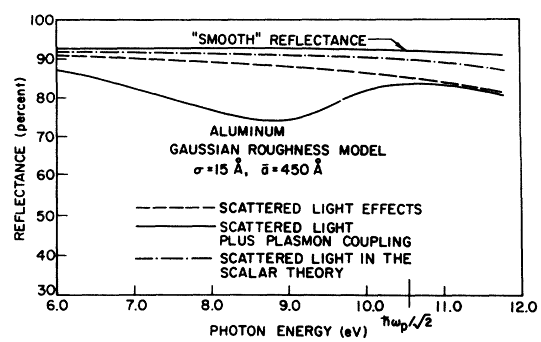

FIG. 2. Surface-roughness-induced reflectance drops in Al (theory of Elson and Ritchie), assuming a Gaussian surface-roughness autocorrelation function characterized by rms roughness $\sigma = 15$ Å and autocorrelation length $\bar{a} = 450$ Å. The reflectance drop is broken up into scattered-light-induced and plasmon-induced components; also shown is the scattered light in the "scalar" scattering theory.

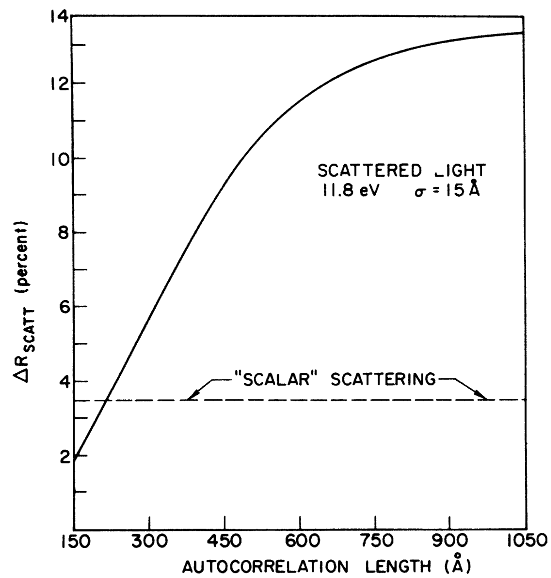

FIG. 3. Scattered light in the Elson-Ritchie theory. The sensitivity of scattered light to the surface-roughness autocorrelation length is compared to the lack of sensitivity of scattered light to this parameter in the "scalar" scattering theory. A Gaussian roughness model is assumed.

component at 11.8 eV for a Gaussian distribution characterized by $\sigma = 15$ Å and various autocorrelation lengths. This plot qualitatively confirms the dependence discussed above and indicates how scattered-light components for various values of the autocorrelation length compare to the scattered light expected in the scalar theory. The Al optical constants used in these curves were obtained from the experimental reflectance of smooth Al films in a manner described in Secs. III and IV.

In the actual application of the above expressions for the plasmon-induced ΔR_{sp} and scattered-light-induced ΔR_{sc} reflectance drops, a modification was made as suggested by Ritchie.[10] The effects of the absorption and scattering of light on the strength of the exciting photon field were accounted for in a manner which allowed application of the theory over a larger range of reflectnace drops. It was assumed that ΔR_{sc} and ΔR_{sp} could be more appropriately expressed as

$$\Delta R_{sc} = (e^{\Delta R'_{sc}} - 1)\, e^{-\Delta R_{tot}}\,, \qquad (7)$$
$$\Delta R_{sp} = (e^{\Delta R'_{sp}} - 1)\, e^{-\Delta R_{tot}}\,,$$

where $\Delta R_{tot} \equiv \Delta R'_{sc} + \Delta R'_{sp}$, and $\Delta R'_{sc}$ and $\Delta R'_{sp}$ are the theoretical expressions for the reflectance drops implied in Eqs. (3), (5), and (6).

The above theories of Ritchie and Elson thus provide a technique to account for both roughness-aided absorption of energy by surface plasmons and roughness-aided scattering of incident photons in terms of arbitrary surface-roughness spectra. One important process noted in the specialized theory of Hunderi and Beaglehole[8] but not extended to arbitrary surface spectra is the roughness-induced anomalous absorption associated with the finite ϵ_2 in real metals. The nearly free-electron nature of Al, $\epsilon_1 > \epsilon_2$ over the frequency range of interest, offers reasonable justification for believing that this effect is small in Al. The clear-cut experimental evidence reported in Paper II provides the best argument for ignoring such anomalous absorption, in that roughness-induced increases in photoyield (and presumably increased absorption) die off drastically above the surface-plasma frequency. This indicates that the dominant mechanism for absorbed light is through surface-plasmon excitation.

One final process that extends beyond the theory described in this paper is light scattering through surface-plasmon reradiative decay, as developed by Hunderi and Beaglehole.[15] Such a process is effectively proportional to σ^4 and thus of higher order than the σ^2 processes that govern light scattering and plasmon excitation. We have observed no strong experimental evidence (such as roughness-dependent plasmon broadening or decreases in photoyield per absorbed photon), however, to indicate roughness-induced reradiation.

C. Real Surface-Roughness Spectra: Their Mathematical Models and Determination

In the preceding theoretical expressions, surface roughness has been expressed in terms of an arbitrary roughness spectrum $\sigma^2 g(k)$. In the past, specific functional dependences have been assumed for $g(k)$. The most commonly used roughness model has been the Gaussian[1,2,20,22] (explicitly in the "scalar" scattering theory) and also the Lorentzian and exponential models[2,3] for the autocorrelation function. All three models are similar in that their surfaces are completely specified by a rms height variation σ and an autocorrelation length $\bar{a}$.

Experimental studies have dealt with the measurement of scattered light on rough surfaces, and the "scalar" theory has often been employed. Attempts to fit, say, a Gaussian roughness model to experimental results within the "scalar" scattering theory have proved reasonably successful. With more sophisticated theories of light scattering and plasmon excitations and with the measurement of reflectance into the far uv as is reported in this paper, fitting of experimental results to a two-parameter surface-roughness model becomes more difficult. Equivalently, the theoretical reflectance drops predicted by a given σ and $\bar{a}$ value become increasingly sensitive to the exact roughness model used (see Fig. 4). This inability to yield agreement with experiment in terms of a simple surface model

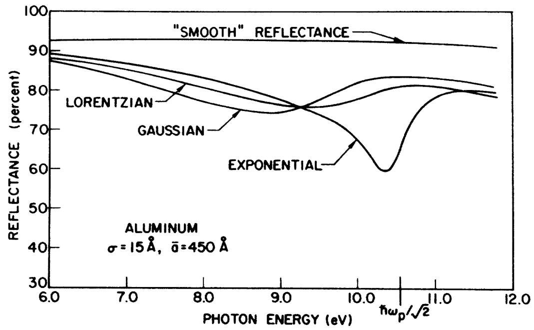

FIG. 4. Surface-roughness-induced reflectance drops in Al (theory of Elson and Ritchie). Plots of three mathematical models of surface roughness are characterized by a common $\sigma = 15$ Å and $\bar{a} = 450$ Å.

implies that a great deal more information concerning actual surfaces can be obtained by analyzing experimental results in terms of the more sophisticated light-scattering and plasmon-coupling theories. A primary purpose of the present reflectance studies is to confirm the validity of recent theories and to determine to what extent existing theory and experimental uv reflectance studies can be applied to establish the actual roughness spectra of nearly free-electron metals such as Al.

Generally, rough surfaces have been characterized only by a rms height variation σ; even specifying an autocorrelation length has been difficult. The Bennett-Porteus[20] "scalar" scattering theory has been used by Bennett and others to determine σ from reflectance drops in the visible and near infrared reflectance of metals. In this range, the assumption that $|\epsilon_1| \gg 1$ is valid; $\bar{a}$ may be comparable to λ in certain surfaces and, if surface-plasmon excitation is not a donimant cause of reflectance drops, reasonable values for σ could be obtained.

Such roughness-measurement techniques were employed in the first studies of surface-plasmon-induced reflectance drops in an attempt to characterize the rough surfaces. Stanford *et al.*[4] investigated the reflectance of silver on roughened surfaces whose rms height variations later were estimated by overcoating the Ag films with Al and by measuring reflectance drops in the visible. The Al overcoat removed the surface-plasma frequency well away from the frequency of measurement, and it was assumed that observed reflectance drops were caused by roughness-induced light scattering as described in the "scalar" theory. The results of these studies are shown in Fig. 5. One significant point regarding these results is that the surface-plasmon coupling is extremely well correlated to the measured rms roughness for these Ag films. This does not occur in all metals. To appreciate why this correlation is so strong, note that the measured surface-roughness correlation lengths have been on the order of 1000 Å.[23,24] Figure 6 is a plot of a Gaussian roughness spectrum characterized by such an autocorrelation length and also contains the surface-plasmon dispersion relationships of Ag and Al. It can be seen that surface-plasmon excitations near the surface-plasma frequency of Ag occur for relatively small ($0.2-0.3\times10^{-2}$ Å^{-1}) surface momenta values and in a momenta range where the surface-roughness spectrum is still appreciable. The Ag surface-plasmon excitation thus results from surface-roughness components that sample the roughness in the low-k region, which accounts for most of the area under the $g(k)$ curve. The magnitude of this component therefore is propor-

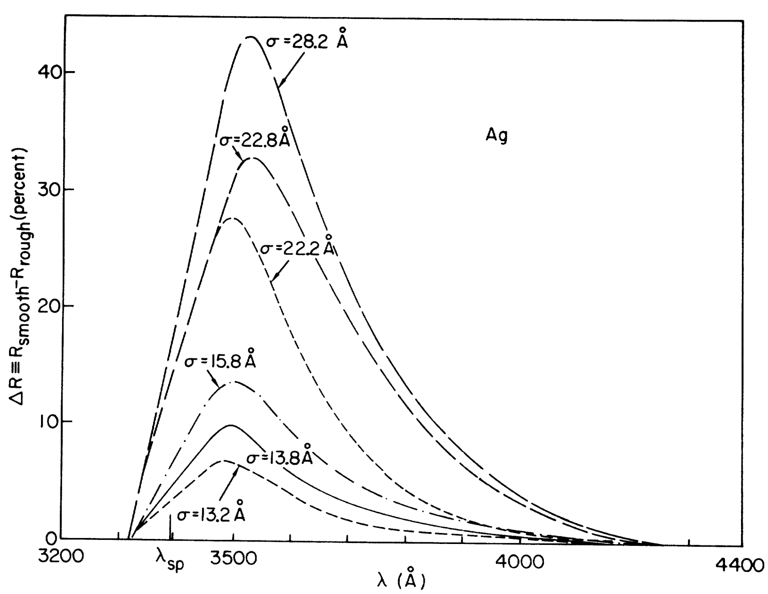

FIG. 5. Experimentally observed reflectance drops in Ag as a function of surface roughness σ (Stanford *et al.*).

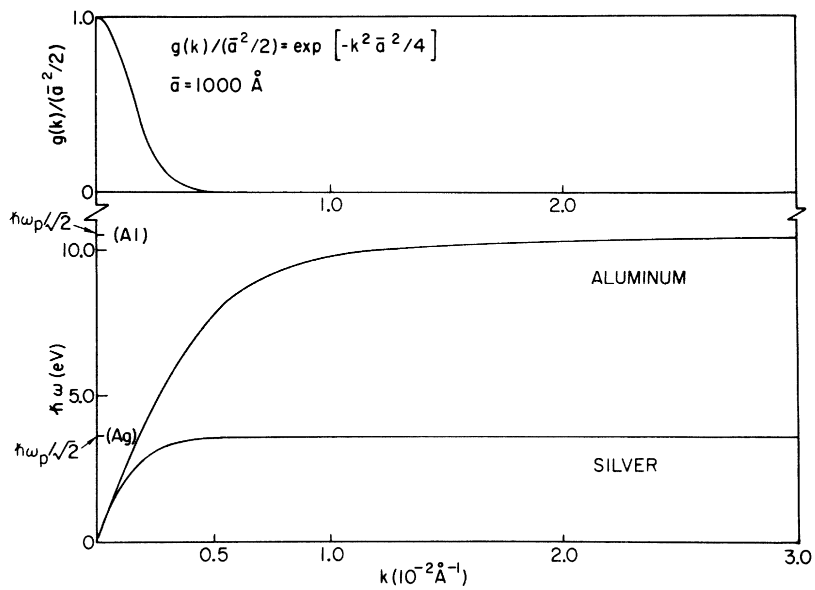

FIG. 6. Comparison of a Gaussian surface momentum distribution vs k, with surface-plasmon dispersion curves of Al and Ag. Correlation length $\bar{a}$ is 1000 Å.

tional to σ if $\bar{a}$ does not vary appreciably from surface to surface.

Two observations are noteworthy when comparing the Al dispersion curve to the Gaussian roughness spectrum. The first is that the surface momenta components involved in plasmon excitation are well removed from the large area of $g(k)$ contributing to the total roughness σ. The plasmon-exciting components lie far out on the tail of the spectrum, and any strong correlation between surface-plasmon excitation and rms roughness becomes somewhat fortuitous. The second is that, although both roughness-scattered and plasmon-absorbed light in Ag arise from only low-k roughness components, scattered light and plasmon absorption in Al result from both low- and high-k components, which implies that much more information concerning roughness spectra can be obtained from the simple reflectance measurements of Al than can be obtained from Ag.

III. EXPERIMENTAL STUDIES

A. Evaporation Techniques and Preparation and Determination of Surface Roughness

1. *Evaporation Techniques*

The sensitivity of reflectance measurements of Al to surface contamination is well known and has been discussed extensively in the literature[11–14,25]; consequently, the present series of experiments must be carried out at low enough pressures so that such contamination effects could be eliminated totally. A Varian Vacion combination pump and high-vacuum uv reflectometer[26] were used for the reflectance measurements described in this section. In each experiment, 45 cm of 0.010-in. 99.99% Al wire were evaporated from a 0.020-in. W filament. In all cases, evaporation pressures were $\leq 1\times10^{-8}$ Torr and base pressures were generally $\leq 5\times10^{-11}$ Torr; kinetic-theory calculations reveal that these pressures were low enough to ensure contamination-free surfaces, with H_2 monolayer periods on the order of 8 h, assuming a unit-sticking coefficient. In the preparation of rough surfaces, evaporation rates were 7–10 Å/sec, although rates as high as 55 Å/sec were used to produce smooth surface films. All films were in the 800–1000-Å thickness range, and these values were determined by employing a quartz crystal gauge.[27]

2. *Preparation and Determination of Surface Roughness*

Virtually none of the roughness preparation and measurement techniques described in this section would have been possible without the suggestions and cooperation of Bennett and Stanford.

Any meaningful measurements of the roughness-dependent reflectance of Al must depend on our ability to vary and measure such roughened surfaces. To vary surface roughness, the method used was to overcoat our float-glass substrates with films of CaF_2, as first suggested by Bennett *et al.*,[28] and then the Al films were deposited over these CaF_2 roughened substrates. Depositions of CaF_2 were carried out at the Michelson Laboratory, and CaF_2 film thicknesses were varied from 900 Å in experiments for which Al film rms roughness was later found to be ~15 Å to thicknesses of 2650 Å in experiments for which rms roughness was found to approach 30 Å.

The assumption made in the above technique was that the metallic deposition will follow the contours of the CaF_2 on which it is deposited. Although Bennett has found that Ag surface roughness correlates reasonably well with the CaF_2 roughened substrates on which the Ag is deposited, we had no *a priori* reason to expect such correlation in Al depositions. Johnston *et al.*,[29] for example, have compared scattered-light values from Al and Au films irradiated in the far uv (1216 Å). Their results indicated that, although scattered light from Au films was correlated quite well to substrate roughness for Au film thickness out to 3000 Å, scattered light from the Al films rose sharply from the substrate value for Al film thickness greater than 500 Å, indicating that the Al film growth produced a significant additional roughness of its own. Despite these peculiarities in Al film growth, our experimental results (Fig. 8) revealed that the measured Al film roughness was reasonably well correlated to CaF_2 film thickness, and this correlation is probably a result of the comparable Al film thicknesses for the various samples studied.

One of the most serious problems associated with controlled-roughness studies of Al reflectance and photoyield is not so much that of creating surface roughness as it is of eliminating such roughness. It can be seen in the theoretical curves of Fig. 4 and from the experimental results that follow that significant coupling to surface oscillations can exist in films prepared on even the smoothest of substrates for such metals as Al which have plasma frequencies in the far uv and correspondingly short plasma wavelengths. To reduce such coupling, special bowl-feed polished-quartz substrates were obtained from the Michelson Laboratory, and these substrates yielded the smoothest Al films obtainable in our reflectance and photoyield measurements.

The roughness determination of these films was complicated by the high reactivity of Al. Our laboratory has no facilities for measuring σ via highly accurate visible-reflectance measuring techniques, and it was feared that contamination would destroy surfaces in transit if samples were shipped to the Michelson Laboratory for roughness determination. As a solution, we decided to utilize the high correlation of surface-plasmon excitation in Ag to the rms roughness in Ag films. This correlation was implied in the results in Fig. 5 and is replotted explicitly in Fig. 7 as the peak roughness-induced reflectance drop near the Ag surface-plasma frequency vs measured σ.

Our Al films were overcoated with approximately 800 Å of Ag immediately following the reflectance measurement. Because the resultant films were much less sensitive to atmospheric contamination, they could be removed from vacuum for the measurements. From the Bennett and Stanford studies of Ag films deposited on CaF_2 roughened substrates[4,30] we concluded that the Ag overcoat would provide a fairly reasonable replica of the Al surface contours. Reflectance of the Ag overcoated samples was measured over the 3000–4000 Å range immediately following removal of the samples from vacuum. The rms roughness values then were obtained by measuring the maximum surface-plasmon-induced reflectance drop (ΔR_{max} for the Ag overcoat of the Al films) and taking the corresponding σ value directly off the plot of ΔR_{max} vs σ in Fig. 7.

The results of such reflectance measurements for the rough Al films used in the photoyield studies described in Paper II are illustrated in Fig. 8. The relative roughness values determined for the four samples correlated reasonably well with the CaF_2

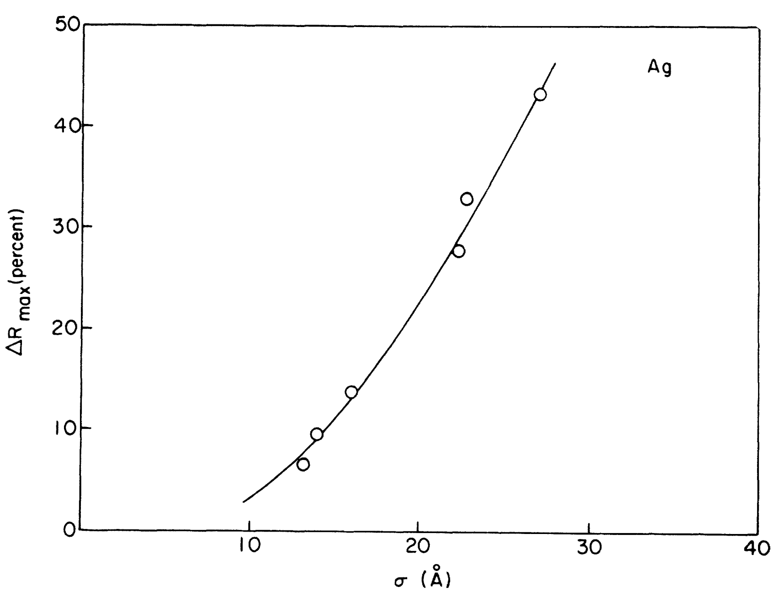

FIG. 7. Plot of ΔR_{max} vs σ for Ag, taken from the data in Fig. 5.

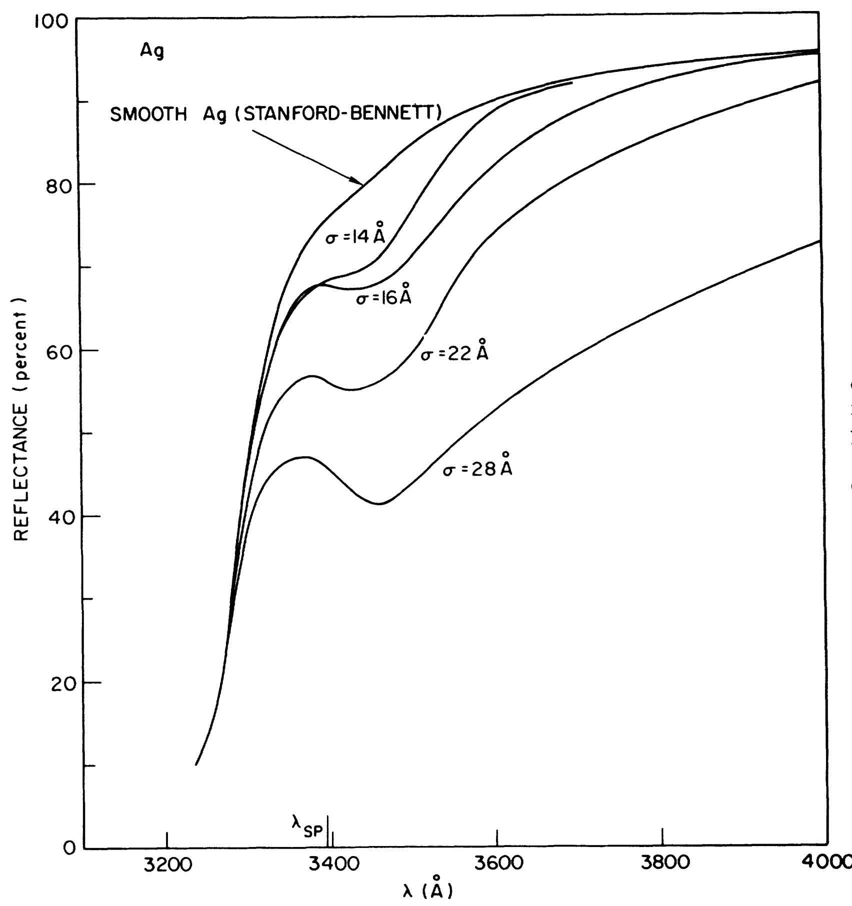

FIG. 8. Reflectance of Ag-overcoated roughened Al samples. Roughness values were obtained by a comparison of maximum deviations from smooth-surface reflectance to the data in Fig. 7.

deposition thicknesses for these samples, the roughest having the thickest (2650 Å) and the smoothest (900 Å) CaF_2 deposition.

Unfortunately, we were unable to apply the above roughness-determination technique to our smoothest films deposited on bowl-feed polished-quartz substrates although the roughness values of these special substrates have been found (by Bennett) to be in the $\sigma = 8-12$ Å range. Our measurement technique is not sensitive enough to measure values of σ below 12–14 Å and, even for higher roughness values, should be considered merely as the best available means of determining Al film roughness rather than as an exceptionally accurate method.

B. Reflectance Measurements of Roughened Al Films

The actual Al reflectance measurements taken in the present series of experiments are shown in Fig. 9, labeled according to their subsequently measured rms roughness. The three roughest films were deposited on CaF_2 overcoated float-glass substrates; the 12-Å film was deposited on a clean float-glass substrate, and the highest reflectance curve was from a film deposited on a bowl-feed polished-quartz substrate. All films except the smoothest were deposited at deposition rates and pressures discussed at the beginning of this section. The smooth film was deposited at approximately 50 Å/sec at 7×10^{-9} Torr and was annealed at 200–400 °C for 2 min following initial evaporation. The annealing process proved crucial and is discussed more extensively in Paper II. All measurements described in Fig. 9 were taken with a highly accurate (± 1%) uv reflectometer described in Ref. 26.

Also seen in Fig. 9 is the smooth surface reflectance of Al determined by Feuerbacher and Steinman.[5] The current smooth surface result is within experimental error of the Feuerbacher result, and there is no valid reason to believe that it is superior; nevertheless, the optical constants $\epsilon_1(\hbar\omega)$ and $\epsilon_2(\hbar\omega)$, so crucial to an understanding of plasmon-lifetime broadening effects, were obtained from our smoothest surface reflectance measurement rather than from the Feuerbacher-Steinman measurement. These constants were obtained by assuming a Drude model for the metal, with $\hbar\omega_p = 14.9$ eV (the experimental value). The scattering time τ was varied to yield a theoretical reflectance curve which agreed with experiment ($\tau = 1.5\times10^{-15}$ sec was

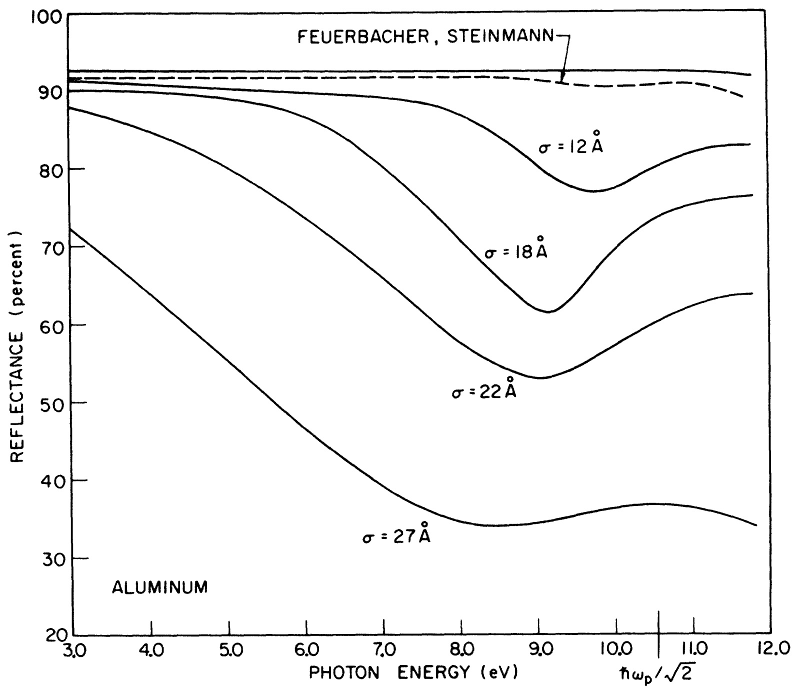

FIG. 9. Al reflectance for films of varying roughness. The rougher films are characterized by their measured rms roughness σ. Also shown is the smooth surface Al reflectance obtained by Feuerbacher and Steinman.

obtained), and ω_p and τ were used to generate ϵ_1 and ϵ_2.

The qualitative features of the results (Fig. 9) essentially are similar to those of Feuerbacher and Steinman. Reflectance drops are strongly correlated to the surface-plasma frequency, indicating that plasmon excitation is a dominant cause of the reflectance drop. The position of the maximum reflectance drop tends to move to lower energies for slightly rougher films, which is consistent with previous observations[4,5] and interpretations[4] in terms of an effective increase in the rough surface autocorrelation length as the roughness increases. From Eqs. (2) and (3), for example, the calculated reflectance-drop peak position can be shown to be inversely proportional to the autocorrelation length of the mathematical surface-roughness model used in the calculation.

The one distinct advantage of our results over previous Al roughness-dependent reflectance measurements is the determination of approximate surface-roughness values. These values emphasize the strong sensitivity of roughness-aided plasmon and light-scattering effects to surface roughness.

IV. DISCUSSION

Of great advantage to our measurements is the availability of the recent plasmon-excitation and light-scattering theories of Elson and Ritchie.[3,10] It is hoped that our experimental results can confirm these theories and that, in combination, they can be used to derive valuable information concerning the surface-roughness spectra giving rise to the results of Fig. 9.

A. Confirmation

The following questions concern the validity of recent theories: (i) How well do these theories match experimental reflectance for an arbitrary choice of the surface-roughness spectrum $\sigma^2 g(k)$? (ii) How realistic is the resultant $\sigma^2 g(k)$ spectrum? (iii) Does the value for σ, necessary for theoretical agreement with experiment, obtain reasonable agreement with our measured roughness values?

To answer these questions, computer calculations of the theoretical reflectance drops implied in Eqs. (3), (5), and (6) were carried out in an attempt to match the $\sigma = 12$, 18, and 22 Å reflectance curves in Fig. 9. No attempt to match the $\sigma = 27$ Å curve was made because the poor appearance of the surface implied macroscopic scattering that lies outside the present theory, and the extremely large uv reflectance drop indicates that such effects could not be described by our perturbative techniques. Ignoring roughness-aided reradiation of plasmons in this extremely rough surface, for example, would be a gross approximation.

The experimental reflectance was matched only over restricted regions of the uv, as indicated by the solid curves in Fig. 10. As this reflectance approached the smooth surface reflectance, the derived roughness spectra became too sensitive to the exact reflectance values at lower energies. The $\sigma = 22$ Å curve was terminated even before this cri-

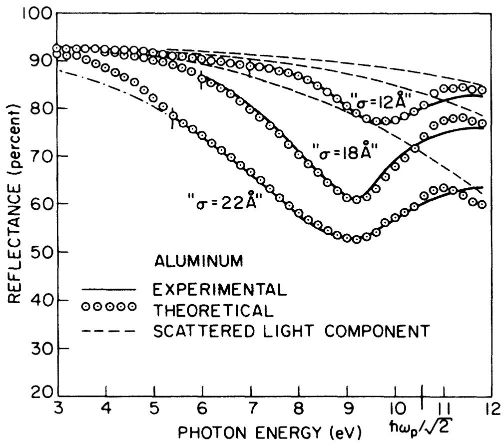

FIG. 10. Comparison of measured Al reflectance to calculated Al reflectance, for rough surfaces (Elson and Ritchie). The roughness spectra were fitted to the experimental data, and plots of these spectra are presented in Figs. 1–13.

terion was met, for reasons described below.

It was evident from our discussion of Eqs. (3), (5), and (6) that surface-plasmon-induced reflectance drops are more or less proportional to the strength of the surface-roughness wave-number component corresponding to the uv excitation frequency (see the dispersion relation of Fig. 1). On the other hand, the reflectance drop associated with light scattering is related to an integral over angle which corresponds to an integral over the low-k spectral components. The scattered-light component in the uv thus yields a great deal of information concerning the roughness components in a spectral region primarily below the spectral region of k space which gives rise to surface-plasmon excitation.

From the Elson-Ritchie theory of coupling to lifetime-broadened surface plasmons, Eq. (3), and from experimental results described in Paper II. it can be seen that coupling to surface plasmons should have terminated appreciably at optical frequencies of 11.8 eV and, as a result, our experimental reflectance drops at 11.8 eV should be considered to stem primarily from scattered light. These scattered-light values impose very strong constraints on the area under the roughness spectra of our experimental films, and these constraints affect the low-k spectral components.

Reflectance drops below the surface-plasma frequency in the curves of Fig. 10 can be caused primarily by surface-plasmon excitation (see Fig. 2). It is seen from Eq. (3) that the strong correlation between a plasmon-induced reflectance drop at a given frequency and the strength of the roughness spectrum at the spectral value corresponding to that frequency can be used to determine directly the strength of the roughness spectrum over spectral values corresponding to the experimental energy range of the curves in Fig. 10. This means that these curves can be used to calculate directly the strengths of the roughness spectra down to energies of 5.4, 6.0, and 7.0 eV for the three films studied. These correspond to spectral components of $k = 0.30$, 0.34, and 0.44 (10^{-2} Å^{-1}).

Roughness spectra for lower spectral components cannot be determined directly because of the inaccuracies in reflectance drops at energies corresponding to these lower spectral values. The values for $\sigma^2 g(k)$ determined at high-k values, however, do impose a constraint on the low-k spectrum if it is assumed that $\sigma^2 g(k)$ must be continuous. If one includes the additional and independent constraint imposed by the scattered-light components of our films at 11.8 eV, then the low-k spectra may be defined totally if the spectra are assumed to be represented by a two-parameter surface-roughness model in this low-k range.

A Gaussian model for the low-k region was assumed, and σ, $\bar{a}$, and the high-k spectral components were computer varied to yield a surface-plasmon-induced reflectance drop which, when added to the associated scattered-light reflectance drop, produced a total reflectance drop in good agreement with experiment. To determine these spectra, the programs were reiterative so that completely self-consistent continuous spectra were

TABLE I. Comparison of the experimentally determined σ values of our films to the values associated with the spectra derived from a theoretical fit of the Elson-Ritchie theory to experiment. Also shown are the Gaussian parameters σ and $\bar{a}$, which characterize the low-k region of the derived spectra. The scattered-light components at 11.8 eV predicted from the derived values for σ in the Elson-Ritchie theory are compared to the scattered-light components predicted for these same σ values in the "scalar" scattering theory.

Experimentally determined roughness (Å)	Roughness from a theoretical fit (Å)	Gaussian model		Scattered light at 11.8 eV	
		σ (Å)	$\bar{a}$ (Å)	Elson-Ritchie (%)	Scalar (%)
12	13.8	12.1	918	6.5	2.6
18	19.3	14.7	744	12.3	6.5
22	27.7	37.7	378	28.8	13.1

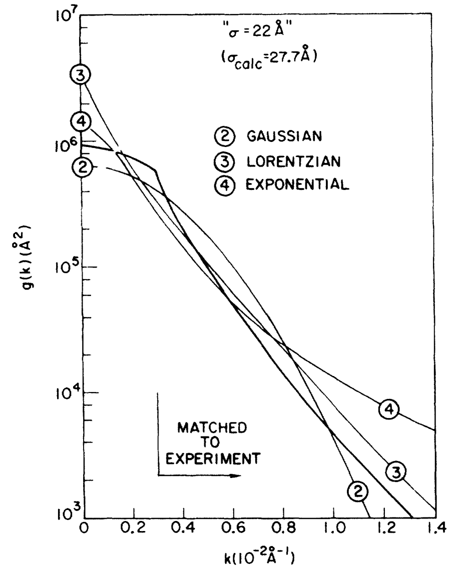

FIG. 11. Normalized surface-roughness spectrum $g(k)$, obtained by fitting the theoretical Al reflectance to the experimental reflectance of the film whose rms roughness σ was measured at 22 Å. The rms roughness of the derived spectrum was found to equal 27.7 Å. Also shown are three normalized mathematical roughness models having the same autocorrelation length as the low-k analytical model for the derived spectrum. The high-k spectrum was matched directly to experiment and is nonanalytic.

eventually achieved. Table I lists the final parameters σ and $\bar{a}$ of our Gaussian model for each experimental film.

The derived spectra then could be used in conjunction with Eqs. (3), (5), and (6) to yield the theoretical curves, plotted as circles in Fig. 10; the dashed curves correspond to the scattered-light portion of the theoretical reflectance drop. Figures 11–13 are plots of the normalized derived roughness spectra $g(k)$, and their configurations are discussed extensively in Sec. IV B.

The derived values of the three roughness spectra were integrated over all k. The square roots of these integrals represent the rms height variation σ. The values obtained for σ are compared to the experimentally estimated values in Table I.

It can be observed that the light-scattering and plasmon-excitation theories of Elson and Ritchie are in exceptionally good agreement with experiment and that the derived roughness spectra required to produce good theoretical results have associated rms height variations that are reasonably close to our estimated roughness values. Differences occurring between the theoretical and experimental curves in Fig. 10 appear in two regions. At higher values of $\hbar\omega$, systematic differences occur between theory and experiment, associated with what appears to be a theoretical surface-plasmon lifetime broadening which is considerably less than the actual broadening. This results in calculated surface-plasmon reflectance drops that die off more rapidly above $\hbar\omega_p/\sqrt{2} = 10.55$ eV than do the experimental reflectance drops. The optical constants used in the theoretical broadening calculations are believed reasonably accurate, and it has been suggested by Ritchie[10] that this problem can be associated with elastic-scattering-induced lifetime broadening of the plasmons. This, and other explanations, are discussed in Paper II, where experimental evidence is much stronger.

At energies below 5.4 eV, a substantial divergence can be seen between the calculated and experimental reflectance curves for $\sigma = 22$ Å. It was found that these curves could not be forced to match below this energy consistent with the restrictions that the k spectrum be monotonically decreasing from $k = 0$ and that the calculated scattered light at 11.8 eV be in agreement with experiment. It is believed that macroscopically scattered light may lower the Al reflectance over the entire spectrum, but such scattering lies outside our scope. Both plasmon-aided and scattered-light reflectance drops implied in the current theory die off rapidly at lower frequencies, and any attempt to fit theory to an experimental reflectance drop rising from some other mechanism would force unreasonably large values for the low-k roughness spectrum. Such effects would be less severe at higher frequencies. Thus, the failure to correct for macroscopic

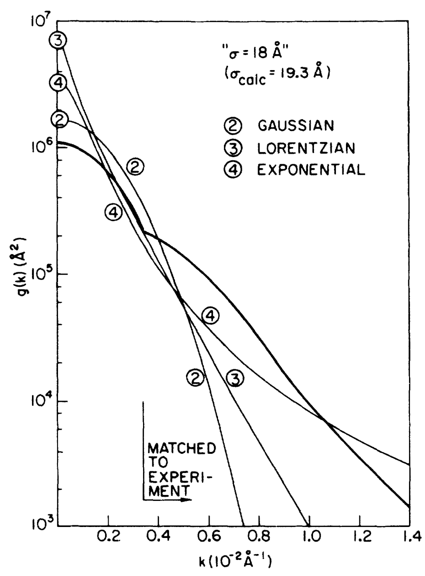

FIG. 12. Normalized surface-roughness spectrum $g(k)$, obtained by fitting the theoretical Al reflectance to the experimental reflectance of the film whose rms roughness σ was measured at 18 Å. The rms roughness of the derived spectrum equals 19.3 Å.

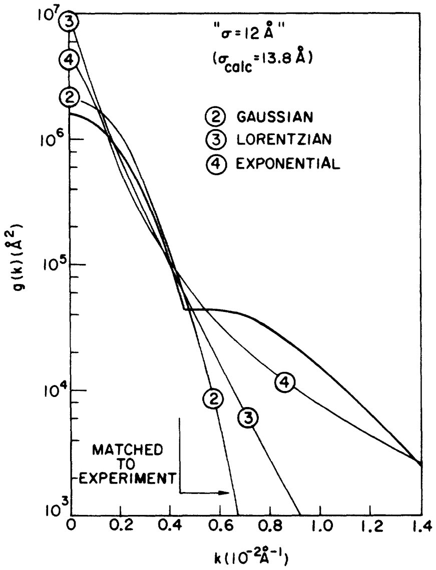

FIG. 13. Normalized surface-roughness spectrum $g(k)$, obtained by fitting the theoretical Al reflectance to the experimental reflectance of the film whose rms roughness σ was measured at 12 Å. The rms roughness of the derived spectrum equals 13.8 Å.

scattered-light components in the $\sigma = 22$ Å film at energies above 5.4 eV makes the exact magnitude of our derived roughness spectrum somewhat suspect but leaves it qualitatively accurate. The termination of our match at 5.4 eV was arbitrary, although it was found that the total theoretical roughness of our derived $\sigma = 22$ Å spectrum did not deviate appreciably from its 5.4-eV value of 27.7 Å as the termination was moved to frequencies higher than 5.4 eV. This insensitivity of the $\sigma = 22$ Å roughness spectrum to the frequency at which the experimental and theoretical match was terminated (for terminations $\geqslant 5.4$ eV) implies that the resultant spectrum is reasonably accurate.

Perhaps the most surprising and interesting implication of the agreement obtained between our experiments and the Elson-Ritchie theory is that roughness-aided scattering of light in the far uv is appreciably greater than had been predicted in the "scalar" scattering theories. This fact is emphasized in Table I which compares the scattered-light components at 11.8 eV for films whose theoretically derived roughness values were 13.8, 19.3, and 27.7 Å to the scattered-light component expected from films of similar roughness values, assuming the "scalar" scattering model. These tabulations imply that, if our measured roughness values are reasonably correct, then the "scalar" theory cannot explain the large uv scattered-light components so easily explained in the Elson-Ritchie theory. It should be noted that an experimental estimate of scattered light is only possible in our study near 11.8 eV. Reflectance drops at lower frequencies are a strong mixture of scattered-light and surface-plasmon effects, making experimental evaluation of the relative merits of the Elson-Ritchie or "scalar" theories impossible at these lower energies.

B. Experimental Interpretation: Determination of Roughness Spectra

The success of the Ritchie-Elson theory implies that much information concerning surface-roughness spectra can be obtained from the reflectance spectra of nearly free-electron-like metallic surfaces. Scattered light in the far uv is greater than had been previously supposed and offers a sensitive means of obtaining information concerning the low-k roughness spectra. For metals like Al, having surface-plasma frequencies in the far uv, additional information concerning high-k roughness components can be obtained from the effects of surface-plasma excitations.

The derived roughness spectra yielding the theoretical reflectance curves in Fig. 10 are shown in Figs. 11–13; also shown are the Lorentzian, exponential, and Gaussian roughness models having the same autocorrelation lengths (see Table I) as the low-k models of our experimentally derived spectra. These common autocorrelation lengths are apparent in the Gaussian model and in the experimentally derived spectrum in the low-k region. The mathematical roughness models and the spectra are normalized so that $[1/(2\pi)^2]\int g(k)\,dk \equiv 1$ and the spectral shapes of the $\sigma = 22$, 18, and 12 Å films can be compared.

The abrupt discontinuities in slope between the low-k Gaussian model and the high-k components that matched directly with experiment are, of course, an artifact of the method used to determine $g(k)$ and, therefore, are unrealistic. Valuable information is, nevertheless, obtainable from these spectra; for example, although the exact values for the k spectra in the region where the Gaussian model was used were sensitive to the exact model (Gaussian, Lorentzian, exponential), the rms roughness [integral over $\sigma^2 g(k)$] was fairly insensitive. The k components between approximately 0.4×10^{-2} and 1.4×10^{-2} Å^{-1} varied by less than $\pm 20\%$, as a function of the type of roughness model used at lower k.

Although not sensitive to the roughness model in the low-k region, the spectra above $k = 1.4\times10^{-2}$ Å^{-1} were sensitive to the initial spectrum values used in our reiterative program because the experimental reflectance drop at $\hbar\omega \approx \hbar\omega_p/\sqrt{2}$ corresponds to an integral over all these high-k plasmons rather than to a single plasmon (as a result of the effects of plasmon-lifetime broadening). The reiterative program thus generates a high-k spectrum whose integral is defined by the experiment but whose shape is defined only by the configuration of the initial spectrum. The derived surface-roughness spectra in Figs. 11–13, therefore, are plotted only in the region of $k < 1.4\times10^{-2}$ Å^{-1}.

Two observations become immediately apparent when comparing these three sets of spectra. The first is that there is no strong evidence that the autocorrelation length increases with increased roughness, as had been previously reported[4,5]; rather, there is evidence of a decrease in $\bar{a}$ for the rougher films. The reasons for assuming $\bar{a}$ increases with σ had been somewhat physical but were based essentially on the experimental observation of an inverse correlation of plasmon-induced peak reflectance-drop position to σ. If it is assumed that rough surfaces can be described by mathematical models, then the calculated reflectance-drop peak positions would be inversely correlated to $\bar{a}$, implying a direct correlation between σ and $\bar{a}$.

It is evident that mathematical roughness models cannot describe our experimental data over the broad spectral range required. Normally, the shape of the actual roughness spectrum in the high-k region that determines the peak position of the plasmon-induced reflectance drop is uncorrelated with the shape of this same spectrum in the low-k region that determines the roughness autocorrelation function. Consequently, no correlation between plasmon-induced reflectance-drop peak position and $\bar{a}$ can be deduced.

The second observation offers an alternative explanation of why the plasmon-induced peak reflectance drops move to higher frequency with lower roughness. It is apparent in Figs. 11–13 that, although the coarse shapes of the normalized derived roughness spectra do not vary appreciably in the low-k region while going from a rough to a smooth film, the magnitudes of these spectra undergo an appreciable increase in the high-k region while moving to smoother films. It should be noted that an increase in high-k components for the *normalized* smooth film spectrum does not imply an absolute increase in the strength of these components; nevertheless, a relative increase in the smooth surface high-k spectra does occur, and it is this shallow slope of the smooth film high-k spectrum that moves the maximum reflectance-drop peak position to higher energy. In Paper II, evidence is cited for high-k components in real surfaces that are much stronger than the components implied in the Gaussian, exponential, or Lorentzian model. These components are attributed to the importance of the discrete stepping of a metallic crystal having a finite lattice constant ($d_0 = 4.1$ Å for Al) when describing real crystals. Such stepping effects should become relatively more significant as σ/d_0 grows smaller or, equivalently, the normalized high-k spectrum should show a relative increase as σ decreases.

This tendency of the roughness spectra to have high-k components that increase appreciably while the low-k spectral shape remains somewhat insensitive to the magnitude of σ emphasizes the very serious limitations of previous attempts to describe surfaces with mathematical models. When $k = 1.4\times10^{-2}$ Å^{-1}, the Gaussian spectrum has dropped far below the experimentally determined spectrum in even our roughest film. In the smoothest film, only the exponential function has a high-k spectrum that comes close to the experimentally determined spectrum. On the whole, recent theoretical developments and measurements that probe the surface spectrum over a broad spectral range make the interpretation of reflectance data (such as reported here) impossible within the constraints of assumed mathematical models for the surface roughness.

In conclusion, some of the assumptions used in deriving the above roughness spectra should be noted. One valid assumption was that $\epsilon_1 \gg \epsilon_2$ is appropriate for Al optical constants in this spectral range. It was further assumed that radiative and nonradiative roughness scattering of excited surface plasmons could be ignored. These processes presumably vary as σ^4, and neglecting them in the smoother films would be appropriate. Anomalous roughness-induced absorption (suggested by Beaglehole and others as arising from finite ϵ_2) also has been ignored partially because ϵ_2 is quite small in Al and partially because the photoyield measurements described in Paper II indicate that surface-plasmon excitation is the dominant source of absorption in rough Al surfaces. In calculating the roughness spectra that gave rise to our experimental reflectance drops, we have disregarded the effects of a $\pm1\%$ reflectometer accuracy on the resultant roughness-spectrum accuracy, but these effects are appreciable for $k \leq 0.44\times10^{-2}$ Å^{-1}. A final assumption is that the acceptance angle of scattered light is 10° in the reflectometer used in our measurements; this value, derived in Ref. 26, was easily incorporated into our scattered-light calculations by integrating from $\theta_c = 10^\circ$ to 90° instead of from 0° to 90° in determining the total scattered-light component. Although this acceptance angle should be included in the present calculations that compare experiment with theory, small uncertainties in the value of the acceptance angle—difficult to determine precisely—do not significantly effect our derived spectra or comparisons.

V. CONCLUSIONS

Ultrahigh-vacuum near-normal-incidence reflectance measurements have been carried out on controlled-roughness films of Al. These measurements provided a highly successful tool for the verification of recent theoretical developments in the theory of light interacting with rough metallic surfaces. The most general of these developments is the Elson-Ritchie[3,10] theory which gives surface-plasmon and scattered-light-induced reflectance drops as a function of the Fourier transform of a surface-roughness autocorrelation function.

Excellent experimental verification of this theory was obtained. The appropriate roughness spectra, $\sigma^2 g(k)$ where $[1/(2\pi)^2]\int_0^\infty g(k)\,d^2k \equiv 1$, could be determined so that theoretical reflectance curves agreed with the experimental curves over virtually the entire energy range of measurement. These derived spectra were found to have associated rms roughness values σ which were in excellent agreement with the measured σ values of our experimental films. The measured σ values were obtained by overcoating the rough Al films with 800 Å of Ag. The drop in reflectance of Ag near its surface-plasma frequency was then compared to the strongly correlated measurements of Ag reflectance drops at these frequencies vs σ (carried out by Stanford *et al.*[4]). Because the Ag films reliably reproduce the contours of the substrates on which they are deposited,[4] this method of estimating the Al film roughness proved reasonably reliable.

The theory of scattered light found in the general theory of Elson and Ritchie was a substantial improvement over the previous "scalar" theory of scattered light. If our experimentally observed scattered-light-induced reflectance drops in the far uv were to be explained in terms of the traditional "scalar" theory of scattered light, it was necessary to assume surface-roughness values that were many times the measured roughness values. This is in marked contrast to the strong agreement between measured roughness values and the values for σ used in the Elson-Ritchie theory to explain far uv scattered light.

Roughness-aided anomalous absorption effects (suggested by Hunderi and Beaglehole[15] and associated with the finite ϵ_2 found in real metals) were not considered, nor were those theories of surface-plasmon radiative and nonradiative scattering. The former effect was discounted because the photoyield measurements described in Paper II indicate that surface-plasmon excitation is almost the exclusive source of additional absorbed energy in roughened surfaces of Al. The excited-plasmon roughness scattering was also ignored because these processes are believed to vary as σ^4, whereas all other processes discussed vary as σ^2.

The notable success of the Elson-Ritchie theory was combined with our experimental reflectance measurements to yield a great deal of information concerning the surface-roughness spectra of Al films. The high surface-plasma frequency of Al allowed the determination of the roughness-spectrum components over a broad range of surface momenta. Normalized spectrum shapes $g(k)$ derived from our experimental results were compared to the two-parameter Lorentzian, Gaussian, and exponential mathematical roughness models. It became apparent from these comparisons that such mathematical models were too restrictive to fit the constraints imposed on the roughness spectra by the uv reflectance measurements and by the more sophisticated theory described in this paper; equivalently, the derived roughness spectra were not well approximated by any of the three mathematical models to which they were compared.

Perhaps the most interesting observation in the comparison between our resultant normalized roughness spectra was that the relative strength of the high-k roughness components increased as one moved from rough to smooth films. The strength of the high-k components in the smoother films was attributed to the possible effects of discrete stepping, which occurs in real crystals having finite lattice constants. The strength of such effects would be expected to increase as the ratio of rms roughness to lattice constant became small.

The most useful aspect of the optical studies reported in this paper is that the results provided an explanation and justification for separating scattered-light- and plasmon-induced reflectance drops in rough surfaces. This separation is critical to the understanding and interpretation of the surface-plasmon-induced photoyield effects discussed in Paper II.

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Study of Aluminum Films. II. Photoemission Studies of Surface-Plasmon Oscillations on Controlled-Roughness Films*

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Photoemission studies have been conducted on Al films of varied surface roughness. Photoyield measurements indicate very strong peaks at energies approaching the Al surface-plasma frequency, and these peak magnitudes are strongly correlated with surface roughness. This photoyield effect has been interpreted in terms of a two-step process. In the first step, surface roughness allows optical excitation of surface plasmons in accordance with recent surface-plasmon excitation theories. In the second step, the excited plasmons decay into one-electron excitations that can be observed in photoemission. Two mechanisms directly analogous to the volume- and surface-photoeffect theories have been proposed for this plasmon-decay process. The anomalously large values of photoyield per decaying plasmon strongly indicate that the historically significant surface photoeffect is the dominant process giving rise to the observed photoyield effects. An experimental estimate was obtained for the characteristic strength of this surface photoeffect. This estimate was confirmed at a single energy (7.8 eV) in an independent measurement of smooth surface Al photoyield vs angle of incidence for p-polarized light. This derived value for the surface-effect strength is believed to provide the first experimental comparisons of the strengths of both surface and volume photoeffects. The high sensitivity of the plasmon-decay process allowed observation of changes in Al photoyield vs time, which were apparently related to changes in film roughness associated with room-temperature annealing. The photoyield effect was highly sensitive to roughness in very smooth films, and a photoyield/(decaying plasmon) approaching 0.3 electrons was observed near the high-k plasma frequency in our smoothest Al films. A mathematical surface-roughness model, based on the discrete stepping of the metallic surface in increments of a lattice constant, was proposed to explain this sensitivity.

I. INTRODUCTION

Although there has been considerable recent interest in both roughness-induced photoyield and roughness-induced optical effects, the main thrust of the studies described in this paper is toward a