$$\Delta_{kl}(z_0) = (l - k) \int_\Omega u_k^* \frac{\partial u_l}{\partial k} dV + i(l - k) D_k(z_0)$$

$$= i(l - k)[D_k(z_0) - Z_k] \; . \qquad (A21)$$

Equation (A19) is quoted in Eq. (2.20) of the text.

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Inelastic Low-Energy-Electron Diffraction for Surface-Plasmon Studies: Extended Measurements on Epitaxial Al(111)[*][†]

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Inelastic low-energy-electron diffraction measurements on a clean Al(111) surface have been greatly extended and improved. This provides the experimental basis for a much more accurate determination of the high-momentum surface-plasmon dispersion and lifetime. The surface is prepared *in situ* in an ultrahigh-vacuum scanning diffractometer by epitaxial deposition on a Si(111) single-crystal wafer. Specular beam inelastic intensity profiles are measured in the $<11\bar{2}>$ and $<1\bar{1}0>$ directions at 15° and 25° incidence. The primary beam energy is chosen to correspond closely to both diffraction-before-loss and loss-before-diffraction processes involving different vestigial Bragg peaks at roughly 50 and 100 eV. Present emphasis is on loss profiles, which have recently been shown to be essentially free of complicating dynamical effects. The use of a 100-meV data grid and a more efficient computer differentiation technique permits determination of loss peak positions to 50 meV under favorable conditions. Internal consistency of the data is demonstrated here and in a more comprehensive analysis by Duke and Landman, published separately. The analysis leads to a substantially different evaluation of the surface-plasmon dispersion than previously obtained. There is evidence that the visibly smoother substrate used in the present work does not affect this result significantly. Experimental procedures and results are discussed in detail.

I. INTRODUCTION

The role of surfaces is critical in many solid-state electronic and optical applications. Device performance often depends on the physical, chemical, and geometrical features which determine the electron-density distribution at the surface. Measurable characteristics of this distribution are therefore of considerable practical interest. Surface plasmons[1] offer such a characteristic in the form of parameters defining the surface-plasmon dispersion and lifetime (SPDL). When the plasmon wave vector $p_{\parallel}$ is small compared to the dimensions of the Brillouin zone[2] the SPDL may be evaluated from optical measurements. The spatial resolution for electron-density variations normal to the surface is quite limited, however, being of the order of $2\pi/p_{\parallel}$. The SPD at larger values of $p_{\parallel}$ has been obtained from the distribution of 34-keV electrons scattered in a Mg foil,[3] but the surface was not well characterized. The surface-plasmon signal using this method is often too weak for precise results.

A more promising method, which is compatible with elastic low-energy-electron diffraction (ELEED),[4,5] Auger-electron spectroscopy,[6] and other surface analytic tools,[7] is based on inelastic low-energy-electron diffraction (ILEED).[5,8-15] Here electrons having ~ 10 – 100-eV energy are involved in an inversive two-step process: (a) An electron loses energy and a related momentum in exciting a surface plasmon; (b) the electron is elastically diffracted backward by the lattice. As a result, each vestigial Bragg peak in the *elastic* intensity vs energy curve (elastic energy profile) of an ELEED beam is accompanied by an *inelastic* intensity distribution which provides information on the surface plasmon. Sections of the inelastic distribution lying in the azimuth of the ELEED beam are called energy, angular, or loss profiles,[9,11] depending on whether the primary energy E, exit (polar) angle θ', or energy loss w, respectively, is chosen as the scanned variable; other variables, including the azimuth ψ and the incidence angle θ, remain fixed. The loss profile is now known to be the most useful data form for determination of the SPDL.[13,14]

Except for a limitation at small $p_{\shortparallel}$,[8] where the optical methods are applicable, ILEED provides the SPDL to $p_{\shortparallel}$ values approaching the Brillouin-zone dimensions. ILEED is, of course, restricted to samples with crystallographically ordered surfaces.

A recent extension of ILEED theory to include multiple elastic scattering, i.e., dynamical effects,[12] has placed new demands on measurement and analytical procedure.[13,14] Except for data on nonspecular beams,[16] which are more difficult to analyze, the only data suitable for determination of the SPDL has been reported by the authors.[11] This was obtained from the (00) beam of a thick epitaxial Al(111) film deposited on a Si(111) substrate. This work is now found to be deficient in the following respects: (i) Emphasis was placed on angular, rather than loss, profiles in which dynamical effects may be neglected; (ii) the data grid (point spacing) and precision are inadequate to take full advantage of the accuracy of the theoretical model; (iii) data is limited to a single azimuth, incidence angle, and Bragg peak, so that no check for internal consistency is possible; and (iv) except for ELEED patterns and energy profiles, no auxiliary sample characterization has been performed.

In the present paper we report a substantially improved set of measurements. Loss profiles have been obtained with a reduction in the data grid to $\Delta w = 100$ meV (effectively 50 meV), $\Delta\theta' = 1°$, and with a factor of $\sqrt{2}$ greater precision in the intensity. Moreover, data have been obtained in both the $\langle 1\bar{1}0\rangle$ and $\langle 11\bar{2}\rangle$ azimuths of the Al(111) surface at 15° and 25° incidence. Primary energies corresponding to two different Bragg peaks in each azimuth have also been explored. Although no additional sample characterization has been performed, results from the visibly smoother substrate used here indicate no effect from large-scale roughness. Substantial refinement in the SPDL result from an enlightened interpretation of the new data. Since the principal analysis is described in the following paper,[15] the present discussion is confined mainly to the discussion of experimental procedure and results.

II. THEORY

ILEED phenomena were first described over forty years ago,[17] but the effects of excitation momenta, which require angular resolution ~1° for observation, were reported only recently.[8] For the surface plasmon the positions of the intensity maxima can be understood roughly on the basis of a simple conservation-law model (CLM).[8,11] The two-step process in this case assumes only conservation of energy and momentum parallel to the surface in the inelastic step and kinematic diffraction in the elastic step. This gives rise to a doublet structure in

the inelastic angular profiles, corresponding to the two possible directions of the surface-plasmon momentum in a given azimuth. Two doublets are predicted, one at the Bragg energy E_B, corresponding to the diffraction-before-loss (DL) process,[17] and one at E_B plus the plasmon energy, corresponding to the loss-before-diffraction (LD) process.[18] Using this model it is possible to translate peak positions in the angular, or loss, profiles into points on the dispersion curve.[11] An inherent practical limitation is the difficulty of locating true peak positions, which are influenced by overlap of the bulk-plasmon[1] peak, and by asymmetry and broadening resulting from the ELEED energy profile, plasmon lifetime, and instrumental resolution. A more fundamental limitation is that the analysis is based on the angular or loss profile exhibiting maximum intensity with respect to primary energy. This results in a dependence on the inelastic energy profiles, which are now known to be strongly influenced by dynamical effects.[12]

A quantum-field-theory model (QFTM) of inelastic diffraction by Duke et al.[9] permits detailed calculation of the various inelastic profiles. Although also based on a kinematical two-step model, this theory predicts details of the intensity modulation which cannot be adequately described in terms of the CLM. In particular, the coherence between DL and LD processes is included. In the case of the bulk plasmon this leads to the phenomenon of "sideband diffraction,"[9] which is believed to have been experimentally observed.[16] However, multiple elastic scattering, which is not included in the theory, can lead to similar effects.[12] For this reason an unambiguous extraction of the bulk-plasmon dispersion from ILEED is difficult or impossible at present. The profiles associated with the surface plasmon are much simpler, since momentum is directed along the surface plane. Here the theoretical profiles, treated as functionals of the SPDL, may be compared with the experimental profiles to determine the best fit. The resulting dispersion,[10] based mainly on the Al(111) angular profiles of Porteus and Faith,[11] agrees essentially with that obtained from the CLM. However, the data permit a wide range of ambiguity in the dispersion parameters.[10,13]

An extension of the theory by Duke and Landman[12,14] to include dynamical effects leads to the important result that only the loss profiles may be treated as nearly kinematic. Here dynamical effects are found to be important only when the resolution in w and θ' are better than 50 meV and 1°, respectively. It is therefore reasonable from a theoretical standpoint to use a smaller data grid than $\Delta w = 400$ meV, $\Delta\theta' = 2°$, used in the authors' original data. The essential experimental limitation is the ratio of noise to amplified collector sig-

nal for a given peak width. Economy dictates a minimum spacing such that the intensity of adjacent data points is significantly different. The effect of instrumental resolution was studied[14] and found to have a negligible effect on peak positions in the loss profiles, thus permitting a direct comparison of theoretical and experimental determinations of these profiles.

III. EXPERIMENTAL PROCEDURE

A. Diffractometer

The diffractometer, which is shown schematically in Fig. 1, is a noncommercial scanning-type instrument. The electron gun contains the following elements and voltages relative to ground: an emission-stabilized tungsten hairpin-type filament 1 $(-E$ V), focusing electrode 2 $(-E-23V)$, extractor 3 $(-E+700$ V), anode 4(0 V). One member of each pair of deflection electrodes 5 – 7 is at ground potential. The voltage on the other may be varied independently or linearly with E for accurate direction of the diffracted beam into the collector over a limited range of primary voltage E. The offset provided by the two vertical deflection pairs 6, 7 performs three functions: It permits the apparent source to be moved slightly out of the fixed horizontal plane of collector rotation to compensate for small dc perturbing fields or minor sample misorientation. It obscures the sample from the hot filament, and it provides some monochromatization. Coarse collimation is provided by a vertically elongated aperture at the end of the drift tube, while fine collimation is accomplished by the two coaxial circular apertures 8 on the front of the collector 9. These select a 2° cone of electrons emerging from a limited area of the sample 10. This cone is directed to the axial region of a tube-diaphragm retarding-field analyzer formed in part by the guard shield surrounding the Faraday cylinder. Electrons having sufficient energy to overcome the retarding voltage E_r applied to the guard shield contribute to the collector signal. E and E_r are each obtained from a well-regulated power supply (Hew-

lett-Packard 6209B) combined with auxiliary voltage regulators, which provide ±5-mV stability over periods of 1 h or more. The direct beam current into the collector with sample removed is typically $\sim 10^{-8}$ A with a measured energy spread of ≤ 1 eV.

The sample goniometer 11 and collector rotate about the same vertical axis, which lies in the sample-surface plane. The former motion varies the angle of incidence θ, and the latter varies the exit angle θ', both angles being measured from the sample normal. The goniometer also permits rotation about the sample normal; this varies the azimuth angle ψ, which is referenced to some arbitrary crystallographic direction in the sample-surface plane. Intensity measurements are restricted to the plane of incidence, i.e., the azimuth defined by the sample normal and incident beam. Continuous ψ and θ' rotation at normal incidence permits a rapid scan of the ELEED pattern. The sample is mounted on a high-purity niobium palette, which may be removed from the goniometer by means of the manipulating rod 12, and withdrawn to position 13 for sample preparation. The rod, which also transmits the ψ rotation to the goniometer, is controlled by rotary and thrust drives 14 and 15. All mechanical drives, including those for the θ' and θ motion, are magnetically coupled through the vacuum envelope with well-concentrated fields, permitting angular settings reproducible to within 0.2°. The electromagnets are either field compensated, or are operated intermittently to eliminate spurious beam deflection. All other parts are of nonferromagnetic materials, principally stainless steel. A freon-cooled 6-in. Orb-Ion pump and baffle provide a field-free working vacuum at 1×10^{-10} Torr or less after bakeout. Helmholtz coils maintain the residual magnetic field in the diffraction region to less than 20 mG.

B. Sample Preparation and Orientation

Details of the sample-preparation chamber 16 used in the present study are given in Fig. 2. The sample S may be rotated 360° to face any of six available vacuum ports. These contain a focused-
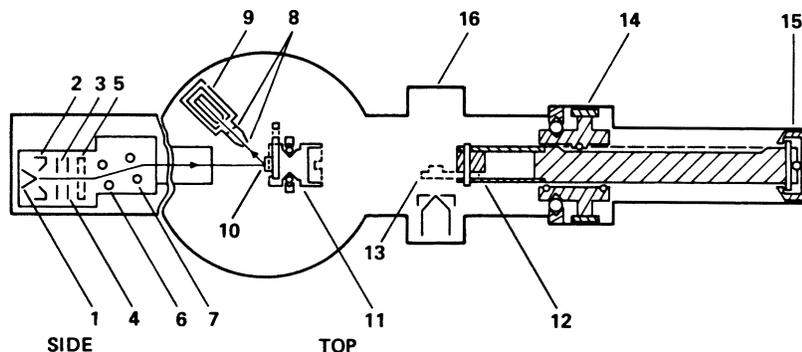
FIG. 1. Schematic of the diffractometer. The electron gun is shown rotated 90° relative to the rest of the apparatus. The goniometer 11 as shown here is set for normal incidence.
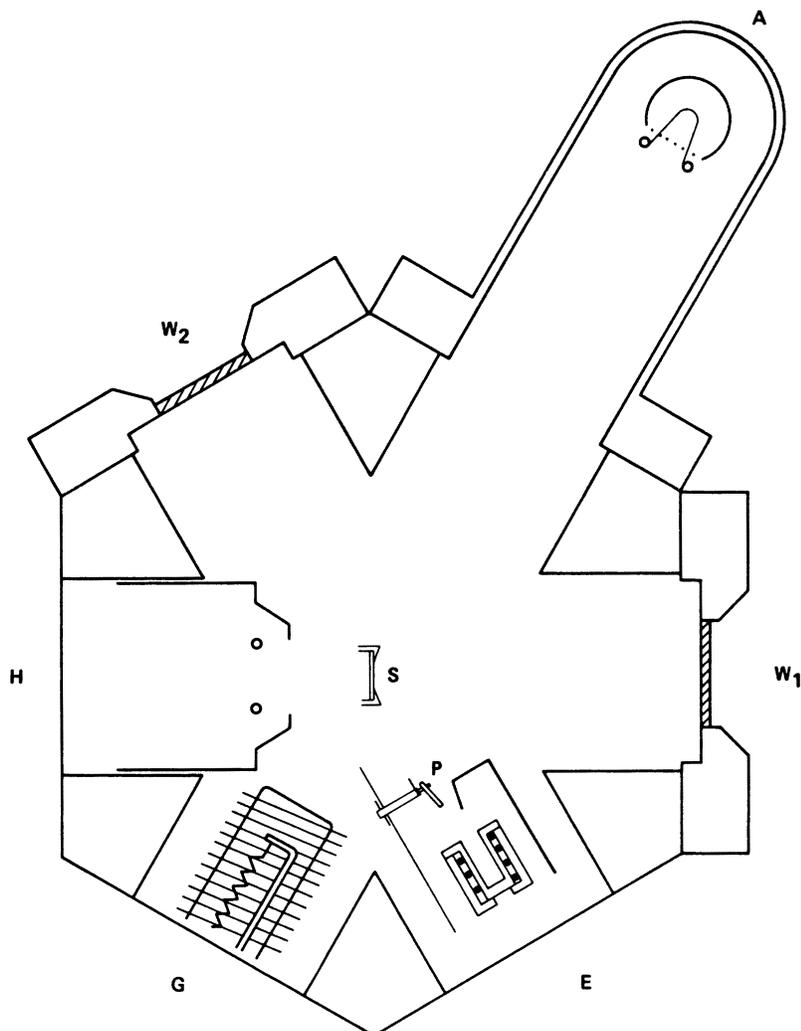
FIG. 2. Sample preparation chamber viewed toward gun end of diffractometer. The lower half of the evaporator shroud, which guides the aluminum charge into the crucible, has been omitted for clarity.

electron-bombardment heater H[19] used only on the back surface; an ion gauge, G; an aluminum evaporator, E; a window, W_1, for pyrometric measurements and for observing the sample during heating and evaporation; a residual-gas analyzer, A; and a second window, W_2, for observing the evaporator. The evaporator consists of a BN crucible, externally threaded to accommodate a helix of 0.010-in. tungsten heater wire, which is covered by a BN sleeve. The charge, consisting of 99.999%-pure aluminum wire, hangs on a pin, P, above the crucible until the latter has been thoroughly outgassed. The pin is then withdrawn by means of the manipulating rod 12 (Fig. 1) permitting the aluminum to drop into the crucible. Deposition rates of up to 100 Å/min can be achieved with pressures in the low 10^{-9}-Torr range as measured by the gauge. Aluminum films produced by a similar evaporator were tested for contaminants in a three-grid LEED system equipped with modulation and lock-in detection for

Auger analysis. With a sensitivity of 1% of the 67-eV aluminum Auger peak,[20] no contaminant peaks were observed up to the 600-eV maximum scanned energy, using 1550-eV exciting energy.

The present sample consists of an Al(111) film grown epitaxially to a thickness of ~ 600 Å on a Si(111) single-crystal substrate. This system was studied by Lander and Morrison,[21] and the preparation technique was developed by Bauer for energy-loss measurements.[22] A new substrate (substrate No. 2) replaces the earlier one (substrate No. 1), which gave a troublesome aging effect attributed to visible changes in surface topography.[11] To minimize this effect the new substrate was cut from a wafer polished by the vendor, using a proprietary chemical-mechanical process. Metallurgical micrographs show little evidence of the irregularities reported on substrate No. 1. Also, no aging was apparent, but some other peculiarities were observed. In particular, good epitaxy can no longer

be obtained without heating in the initial deposition stage, although the "clean" Si(111) 7×7 pattern appears after heating to 1150 °C. Also, nonspecular beams in the Al(111) ELEED pattern show true sixfold intensity symmetry, indicating randomly double-positioned azimuthal orientation of epitaxial crystallites with respect to the substrate. For each day's measurement the old aluminum was reevaporated from the substrate and a new deposition made. Measurements were normally completed within four hours of deposition; repeated data show no evidence of contamination effects at the end of this period. Further details of the preparation are given in Table I.

After deposition the sample is inserted in the goniometer and oriented for measurement. The desired ψ is first set to an accuracy of $\pm 0.5°$ by adjustment of the azimuth rotation for maximum intensity of the corresponding lowest-order nonspecular ELEED beam, as measured in the collector plane. The manipulating rod is then withdrawn and the incidence rotation adjusted until the (00) beam intensity is a maximum at $\theta' = \theta$, the desired angle of incidence.

C. Data Collection

The need for a highly sensitive and efficient data-collection scheme is emphasized by the new demands on precision and resolution. Accordingly, the modulation scheme used in the preceding work[11] was modified to a considerably more efficient com-

TABLE I. Sample preparation.

	Substrate No. 1	Substrate No. 2
Substrate material	Si, Futurecraft	Si, n-type, semimetals
Resistivity	50 Ω cm	1 Ω cm
Thickness	0.016 in.	0.020 in.
Surface orientation	(111) ± 0.005°	(111) ± 0.5°
Polish	abrasive	chem./mech.
Etch	1HF/3HNO$_3$	1HF/3HNO$_3$
Rinse	distilled water, alcohol	distilled water, alcohol
Al deposition rate	100 Å/min	50 Å/min
Al deposition time	6 min	12 min
Preheating	none	600 °C for first minute of deposition
Anneal	400 °C for 10 min after deposition	none

puter differentiation scheme.[23] The basic measurement is the retarding curve in which ψ, θ, E, θ' remain fixed while the collector signal S is measured as a function of E_r. Differentiation of this curve with respect to E_r yields essentially the loss profile. Angular profiles are derived by computer from loss profiles obtained at a sequence of equally spaced θ' values, using data points corresponding to a fixed value of E_r. Inelastic energy profiles can, in principle, be obtained in an analogous way by sequencing E instead of θ'.

Figure 3 is a flow chart of the data-collection system used to obtain retarding curves. The components, starting at the upper left and proceeding clockwise, are as follows: the collector, already described; a Cary model-36 vibrating-reed dc amplifier, which is noise limited at 1×10^{-15} A for a
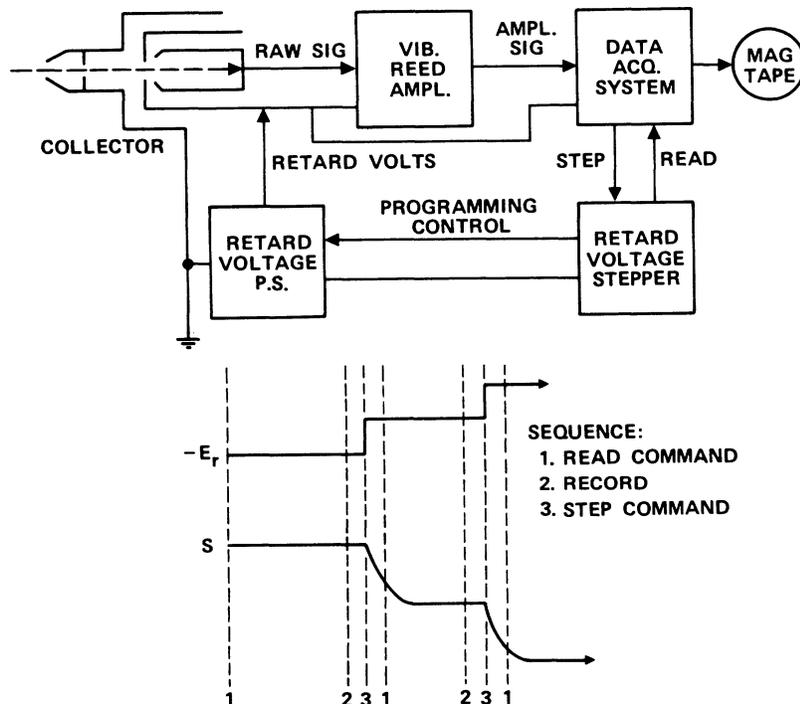
FIG. 3. Flow chart of data-collection system with timing diagram for present measurements.

0.1-sec response time; a Vidar 5203 digital-data-acquisition system (DAS), which converts the amplified analog signal to digital form and records it on magnetic computer tape; a noncommercial voltage stepper containing a programmable sequence of resistances for control of the retarding-voltage power-supply output. The stepper uses conventional scaling circuitry to step through up to 12 binary digits of resistance in a basic unit equivalent to $\Delta E_r = 100$ mV, with an over-all accuracy of better than ± 10 mV in present applications.

The operating sequence for obtaining a retarding curve is described with reference to the timing diagram at the bottom of Fig. 3. Operation starts with a manual read command 1 to the DAS. Following a delay of 0.15 sec, the collector signal at the first level of E_r is recorded at 2, after completion of which the DAS sends out a step command at 3. In response, the stepper advances E_r to the second level and generates a second read command 1. The cycle is then automatically repeated through the final preselected E_r level. At this point the scaler encounters a digit corresponding to zero control resistance, whereupon E_r returns to the first level and the entire scan is repeated. The number of scans, which is determined by the precision required, is controlled by the optional upper scaling limit. Between retarding curves the spectrometer is typically reset to the next θ', which is done automatically on manual command, or to the beginning θ' and the next E if the angular scan is complete.

Data reduction begins with conversion of E_r to w, by requiring that $w = 0$ coincide with the elastic peak in the loss profile as discussed in Sec. III D. The inelastic intensity I per unit w is then obtained by differentiating the collector signal and averaging over the N scans, using

$$I[w_i + (2n\Delta w)^{-1}] = (Nn\Delta w S_0)^{-1}(\cos\theta'/\cos\theta)$$
$$\times \sum_{j=1}^{N} (S_{i+n,j} - S_{i,j}) , \quad (1)$$

where $S_{i,j}$ is the collector signal measured at the loss level w_i in the jth scan. The normalization factor $S_0^{-1} \cos\theta'/\cos\theta$ compensates for variations in the direct-beam collector signal S_0 with E, for variation of the collector-viewed sample area with θ', and for variation of the irradiated area with θ. The parameter n, which determines the effective energy resolution, is equivalent to a modulation amplitude in units of the grid interval Δw. In the present scheme n may be selected as necessary *after* the measurement for optimum data smoothing. The flexibility in n is used to reduce the actual Δw from the minimum of 100 meV provided by the stepper to an effective Δw of 50 meV. This is possible because of the $(2n\Delta w)^{-1}$ term in the argument of I, and is achieved by superimposing the results

of two separate data reductions, where n is first set equal to an odd, and then to an even integer. Consecutive integers are used to avoid a significant difference in the effective energy resolution. Error bars corresponding to $\pm$ the standard deviation σ_I in I accompany each data point in the computer-generated plots, where[24]

$$\sigma_I[w_i + (2n\Delta w)^{-1}] = (n\Delta w S_0)^{-1}(N-1)^{-1/2}(\cos\theta'/\cos\theta)$$
$$\times \left\{ N^{-1} \sum_{j=1}^{N} (S_{i+n,j} - S_{i,j})^2 \right.$$
$$\left. - N^{-2} \left[\sum_{j=1}^{N} (S_{i+n,j} - S_{i,j}) \right]^2 \right\}^{1/2} .$$
$$(2)$$

Observe that σ_I is derived from the reproducibility of I between successive scans, and does not include systematic errors.

After each deposition and before inelastic measurements are made, the elastic energy profile of the (00) beam is always scanned. This serves as a uniformity control on the sample quality and goniometer settings, as well as providing necessary information for the SPDL analysis. The elastic intensity is taken as the collector signal with $E_r = 5.4$ V to exclude the inelastics and secondaries. With the collector positioned for maximum beam intensity the output of the amplifier is displayed in analog form on an XY recorder as a continuous function of E. A correction for variations in the direct-beam collector signal is performed manually.

D. Instrumental Resolution and Accuracy Limitations

The most critical variables in SPDL determinations are θ' and w. The absolute accuracy with which these variables may be assigned to features in the inelastic profiles is limited mainly by resolution and the effect of systematic instrumental errors. The angular resolution is determined by the combination of incident beam divergence and collector acceptance. The effective incident divergence varies as $\cos\theta/\cos\theta'$, while the collector acceptance is constant. Since the incident divergence component is relatively small ($\sim 0.5°$) for the settings used here, the variation of angular resolution with θ and θ' is correspondingly small. In the specular direction, which is the most important direction for the analysis involving the (00) beam, the total angular resolution is represented by the direct-beam angular profile shown in Fig. 4. The peak of this profile determines the zero of the collector-angle scale. To evaluate the effect of systematic errors in θ' which may result from residual fields the positions of a nonspecular ELEED beam were computed from the sample lattice constant and verified by experiment. Since the beam positions depend on E and θ, the absolute accuracy
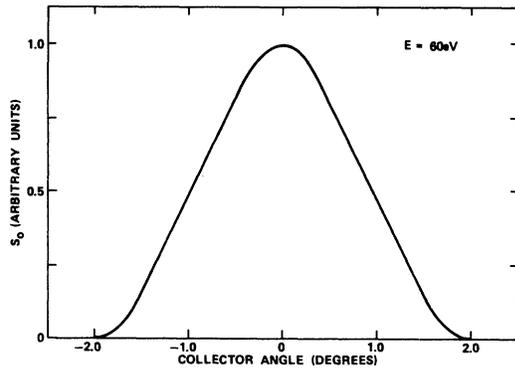
FIG. 4. Angular profile of the direct beam obtained by measuring the direct-beam collector current as a function of collector angle. The sample has been removed from the goniometer and the latter turned to avoid interference.

FIG. 5. Elastic peak in a typical loss profile, showing the relationship to zero energy loss.

of these variables can also be estimated. Internal consistency indicates an absolute accuracy of better than $\pm 0.5°$ in θ' and θ, and better than ± 1 eV in E.

The effective energy resolution depends on the combined effects of diffractometer resolution and the resolution $n\Delta w$ selected for data reduction. Except for a small contribution from inelastic background scattering, these determine the shape of the elastic peak in the loss profile, which is shown in Fig. 5 for $n\Delta w = 0.8$ eV. The absolute accuracy of w (± 0.1 eV) depends on how closely $w = 0$ may be chosen to coincide with this peak. The peak differs from $E_r = 0$, also shown, by 0.25 eV as a result of thermionic energy and the difference in effective surface potential of source and collector.

The *relative* accuracy of θ' and w are limited mainly by the signal-to-noise ratio and resolution. In practice these usually are more significant limitations than the reproducibility of the collector setting ($\pm 0.2°$) or the reproducibility of the stepper-controlled retarding voltage (± 10 mV).

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Elastic Energy Profiles

To locate ILEED structure suitable for SPDL determination one must first locate well-defined Bragg (kinematical) peaks in the elastic energy profile. Such peaks can often be identified by their persistence with changing incidence angle. The identification can be verified from theory, where dynamical features may be studied independently.[25,26] Experimental elastic energy profiles are also important for the analysis, where they are used to characterize the theoretical elastic scattering.[10,13]

Figure 6 shows elastic energy profiles of the (00) beam at $\theta = 15°$, $25°$ from Al(111) films on substrate No. 2. The azimuth contains the $\langle 11\bar{2} \rangle$, and an
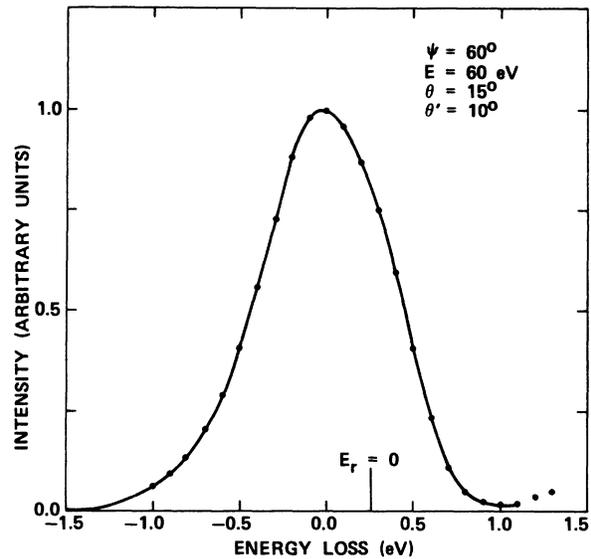
equal mixture of $\langle \bar{1}\bar{1}2 \rangle$ direction, as a result of double positioning. These correspond in Jona's notation,[27] where ψ is replaced by ϕ, to $\phi = 0°$, $60°$; these are equivalent in the (00)-beam profiles by reciprocity.[28] Two prominent Bragg peaks, $E_B = 49, 99$ eV, appear in the $\theta = 15°$ profile. These
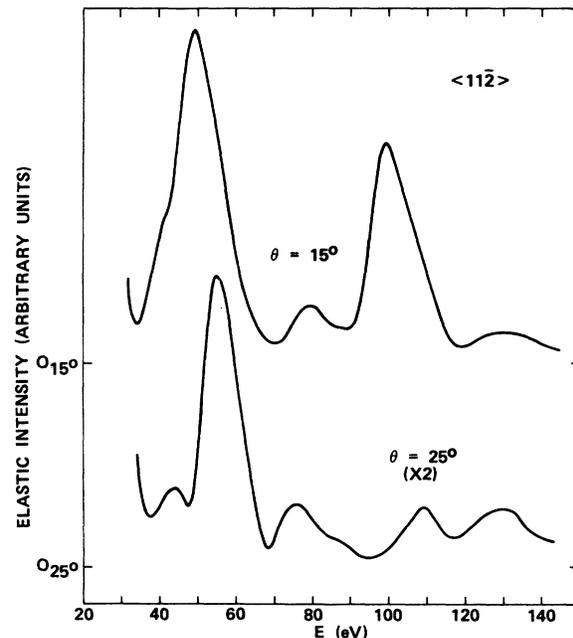
FIG. 6. Elastic energy profiles of the (00) beam from the Al(111) sample used in the present work. The azimuth corresponds to the $\langle 11\bar{2} \rangle$ or $\langle \bar{1}\bar{1}2 \rangle$ crystallographic direction.

energies are slightly lower than previously reported
from substrate No. 1.[11] Subtle differences in peak
shapes are also apparent. In the $\theta = 25°$ profile the
lower energy peak appears at 55 eV, while the high-
er energy peak is suppressed to the extent that it is
not useful for precise SPDL determinations.

Figure 7 extends the above results to the $\langle 1\bar{1}0 \rangle$,
or $\langle \bar{1}10 \rangle$, azimuth, i.e., the close-packed direction.
This is equivalent to Jona's $\phi = 30°$. Bragg peaks
appear at 45 and 102 eV in the $\theta = 15°$ data and at 45
and 117 eV in the $\theta = 25°$ data. In general, peak po-
sitions and shapes observed here agree with those
observed by Jona on single-crystal Al(111) within
the combined absolute error claimed for both sets
of measurements (± 6 eV).

B. Inelastic Loss Profiles

Loss profiles provide the basic data for the SPDL
determinations. Choice of the best values of θ, E,
and θ' for measurement depends on obtaining the
most prominent and, therefore, the most precisely
measurable surface-plasmon loss peaks, which are
at the same time free from influences contributing
to systematic error. For example, it is evident
from Figs. 6 and 7 that choosing a smaller θ tends
to intensify the Bragg peak and, therefore, also the
inelastic structure via the role of elastic diffraction
in the two-step ILEED process. On the other hand,
a smaller θ also tends to enhance the excitation of

FIG. 8. Energy-loss profiles showing the relative
intensity of the surface plasmon ($w \simeq 10$ eV) to bulk
plasmon ($w \simeq 15$ eV) peaks as a function of incidence
angle. The exit angle and primary energy have been
selected in each case to provide the LD surface-plasmon
peak with maximum intensity, shown as unity in the
figure. The two pertinent Bragg peaks, nominally iden-
tified here as 50 and 100 eV, are those appearing in
Fig. 6.

FIG. 7. Elastic energy profiles of the (00) beam from
the Al(111) sample used in the present work. The azi-
muth corresponds to the $\langle 1\bar{1}0 \rangle$ or $\langle \bar{1}10 \rangle$ crystallographic
direction.

bulk plasmons relative to surface plasmons,[1] and
thereby increases interference from the bulk-plas-
mon structure. This is demonstrated in Fig. 8,
which shows the variation in relative intensity of
the surface- and bulk-plasmon peaks in the loss
profiles as a function of θ. By avoiding extreme
values of θ, one can minimize the sensitivity of the
SPDL analysis to uncertainties in the bulk-plasmon
component, and at the same time maintain adequate
intensity for precise measurement.

The intensity of the surface-plasmon loss peak as
a function of E generally exhibits two maxima, one
near the Bragg energy and another near the Bragg
energy plus the plasmon energy. These correspond
to the DL and LD processes, respectively. Al-
though both represent favorable conditions for mea-
surement, the larger value often produces a signif-
icantly better signal-to-noise ratio for the following
reasons: (i) The LD intensity is concentrated al-
most entirely in one member of the predicted angu-
lar doublet, and under present conditions is greater
than the DL intensity; and (ii) the elastic intensity
is less than at the Bragg peak and therefore repre-
sents a smaller collector background current.

Since larger values of $p_{\parallel}$ tend to scatter electrons
at larger angles from the elastic beam, the vari-

able θ' effectively scans the plasmon momentum.[11] Loss profiles representing a range of θ' values including the specular direction $\theta' = \theta$ are therefore desirable. On the basis of observed inelastic intensity, values of θ' somewhat less than θ should be weighted most heavily. Possible interference from the (00) ELEED beam must also be considered when measuring near the specular direction. The presence of an intense elastic component within the acceptance angle of the collector can introduce significant systematic errors[8] in the inelastic intensity, as well as gross noise and instability.

Basic data for the QFTM analysis consists of loss profiles measured and reduced with two different sets of parameters, as follows. Coarse grid: $\Delta w = 400$ meV, $\Delta\theta' = 2°$, $n = 2$, $N = 16$; fine grid: $\Delta w = 100$ meV (effective $\Delta w = 50$ meV), $\Delta\theta' = 1°$, $n = 7$ and 8, $N = 64$. In both cases $\langle 11\bar{2} \rangle$ and $\langle 1\bar{1}0 \rangle$ azimuths were explored at $\theta = 15°$ and $25°$. To permit more time for close spacing of data points and high precision, $E \simeq E_B$ and $E \simeq E_B + 10$ eV only. To provide data for a comparative CLM analysis, which requires more extensive E values, a second set of loss profiles was obtained under the following typical conditions: $\langle 11\bar{2} \rangle$; $\theta = 15°$, $20°$, $25°$; $E_B - 5 \le E \le E_B + 20$ eV, $\Delta E = 5$ eV; $8.8 \le w \le 16.8$ eV, $\Delta w = 1.6$ eV; $\Delta\theta' = 2°$. The modulation scheme[11] of data collection was used, effectively giving $n = \frac{1}{2}$, $N = 32$. Only examples from the QFTM set of data are presented and discussed here.

Figure 9 presents a series of coarse-grid loss profiles with $E \simeq E_B = 49$ eV, where the DL contribution predominates. The effect of SPD is to shift the surface loss peak to larger energy loss as θ' departs from the $15°$ specular direction. Figure 10 presents a similar series where $E = E_B + 11$ eV, giving predominance to the LD contribution from the 49-eV Bragg peak. The greater concentration of intensity in the subspecular direction is characteristic of the LD process. Error bars representing standard deviations, which depend strongly on θ' but are statistically independent of w, are shown for one point in each curve. The greater precision in Fig. 10, as compared to Fig. 9, particularly near the specular direction, demonstrates the advantage of the reduced elastic background intensity. The remaining examples of coarse-grid data, Figs. 11–13, are offered as evidence of the internal consistency of results with changes in Bragg peak, incidence angle, and azimuth. The data are analogous in each case to that of Fig. 10 when allowance is made for variations arising from dynamical effects in the elastic diffraction and from the bulk-plasmon contribution.

The fine-grid data of Figs. 14–16 provide evidence that the dispersion-related shift of the surface loss peak is internally consistent to a much higher level of precision. Representative error
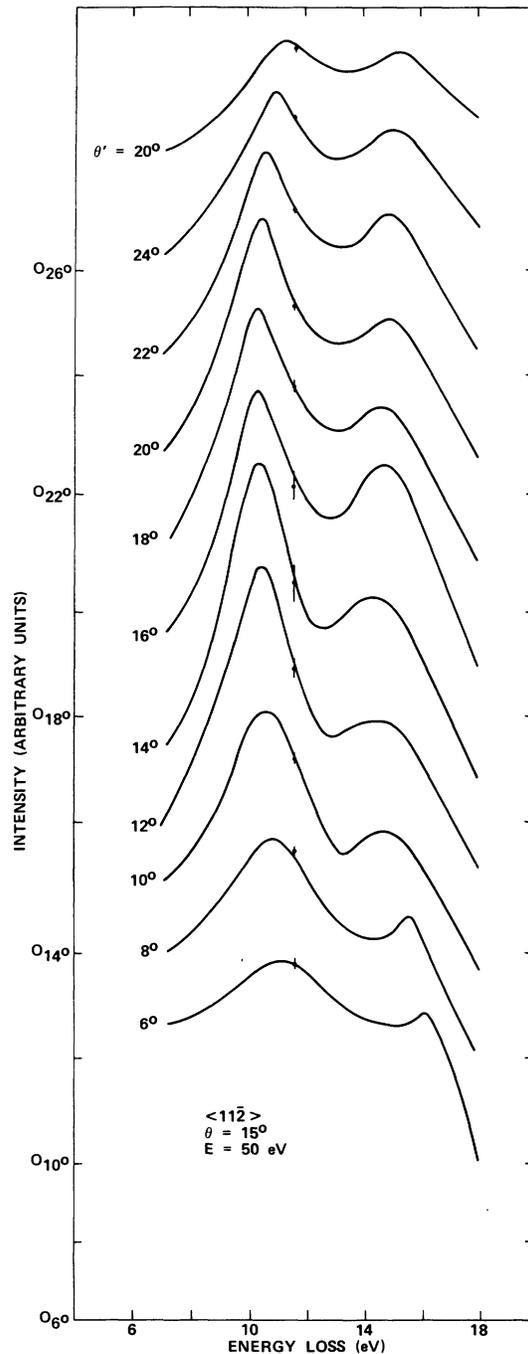
FIG. 9. Coarse grid energy-loss profiles arising predominantly from the DL process in conjunction with 49-eV Bragg peak in the upper curve of Fig. 6. The tick marks along the vertical axis indicate displaced zero levels.

bars, which are again given for each curve, are in some cases smaller than the plotted data points. To illustrate the point scatter all data points are shown for the $\theta' = 11°$ curve in Fig. 15. Under
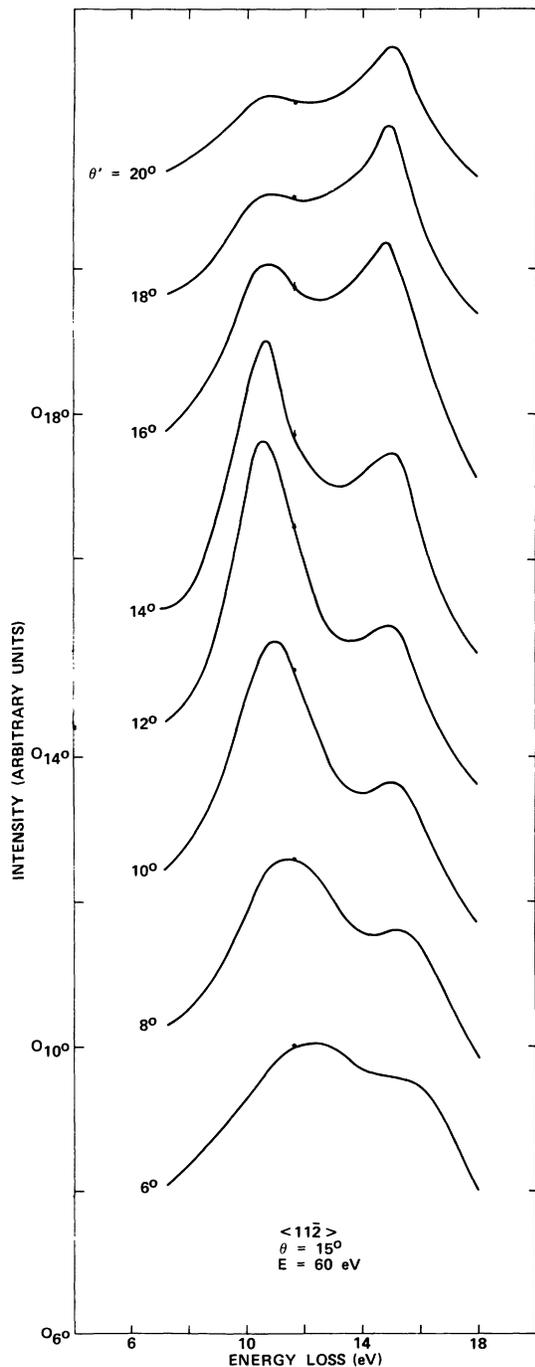
FIG. 10. Coarse grid energy-loss profiles arising predominantly from the LD process in conjunction with the 49-eV Bragg peak.

these favorable conditions relative peak positions can be determined to ± 50 meV.

C. Angular Profiles

Angular profiles provide a means of establishing the incoherent background, [14,15] as well as providing

a check on loss-profile data. Systematic errors produced in the analyzer by an intense elastic background[8] are strongly angle dependent and often can be more easily recognized here than in the corresponding loss profiles. The presence of substantial dynamical effects makes the angular profiles relatively unsatisfactory for SPDL determinations using
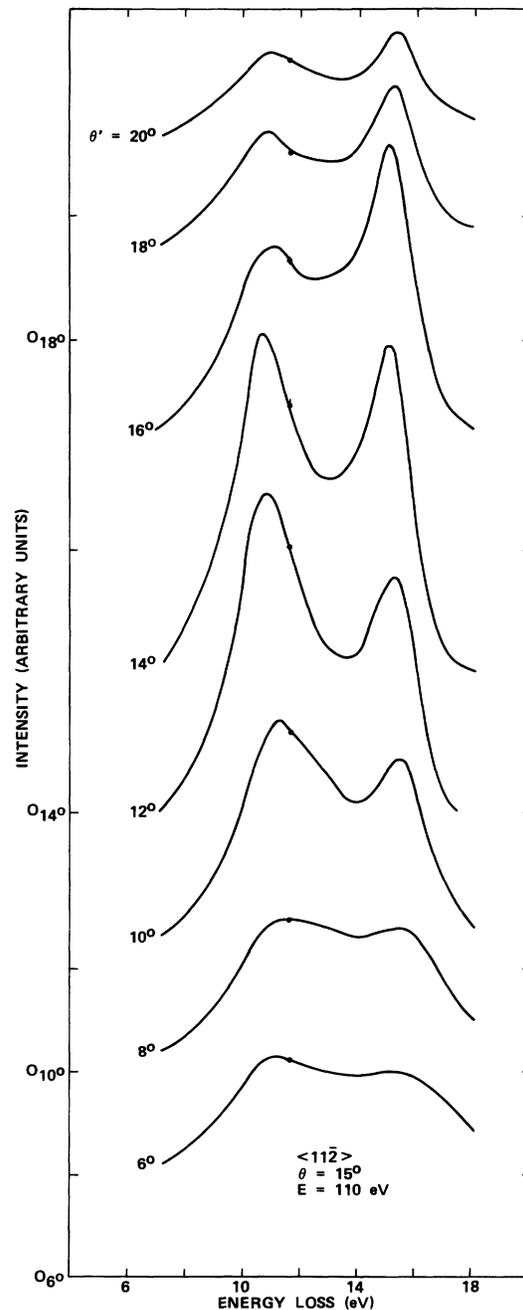
FIG. 11. Coarse grid energy-loss profiles associated with the 99-eV Bragg peak with the LD process predominant.

a kinematic analysis. Ignorance of this fact and consequent misinterpretation of the data has led to erroneous determination of the SPDL in earlier work.[10,11]

Figure 17 presents the data of Fig. 10 in angular profile form. The displayed structure may be interpreted qualitatively in the following way. As a
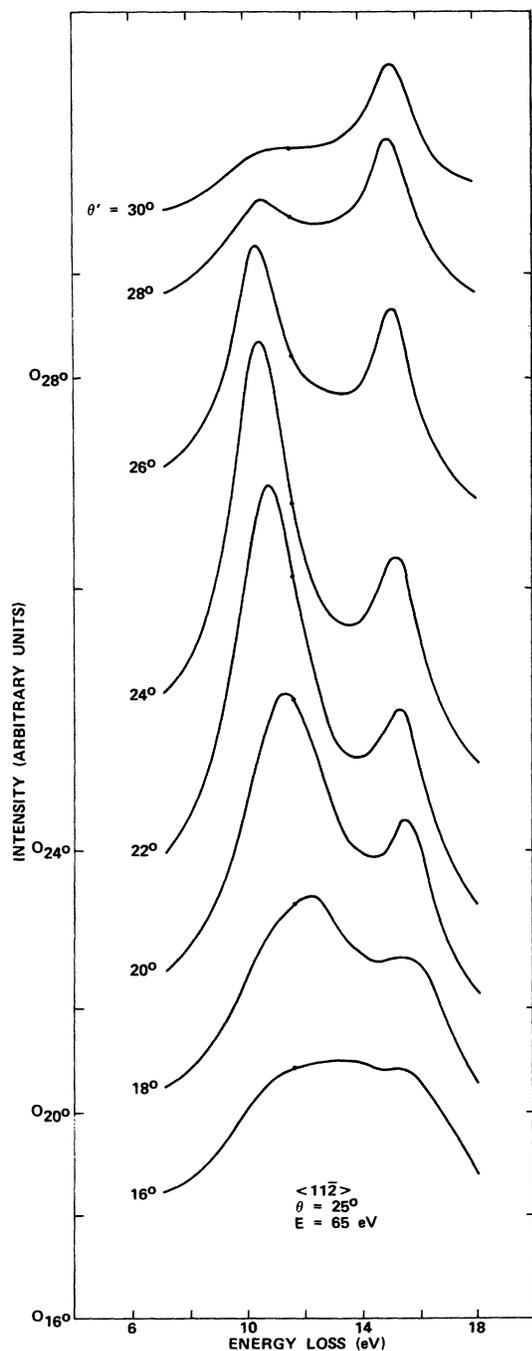
FIG. 12. Coarse grid energy-loss profiles at $\theta = 25°$. The LD process from the 55-eV Bragg peak predominates.
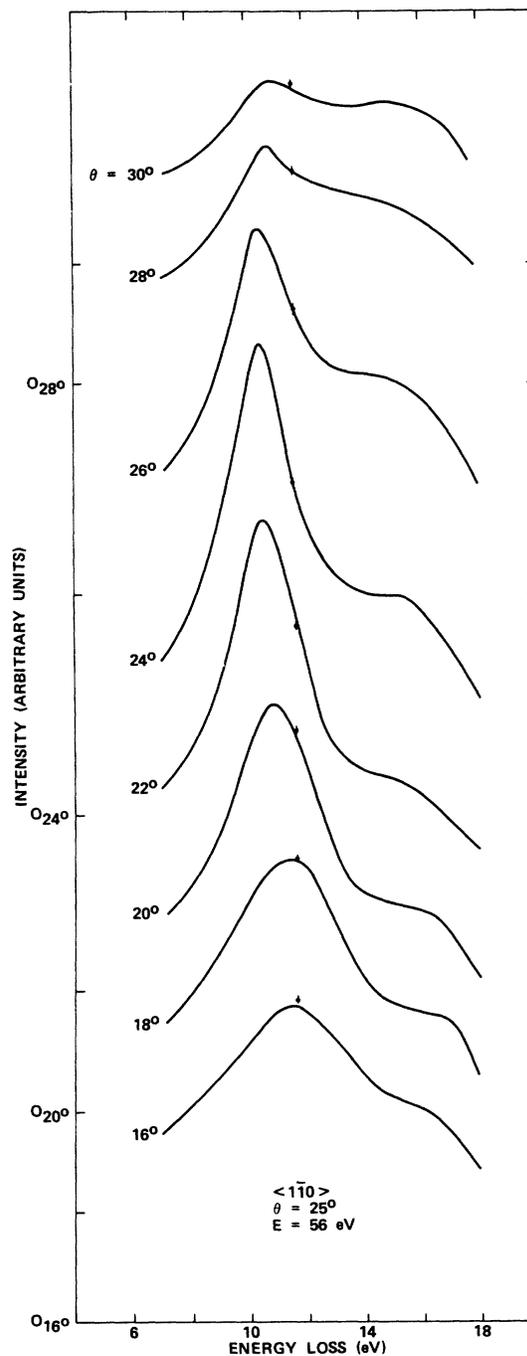
FIG. 13. Coarse grid energy-loss profiles in the $\langle 1\bar{1}0 \rangle$ azimuth at $\theta = 25°$. The LD process from the 45-eV Bragg peak of Fig. 7 predominates.

result of lifetime broadening the surface-plasmon peak appears at the bottom of the figure, at loss values well below the minimum accessible plasmon energy.[8] Proceeding upward, the peak grows with little change in angle until the minimum energy is reached near $E = 10.4$ eV. Beyond this point the
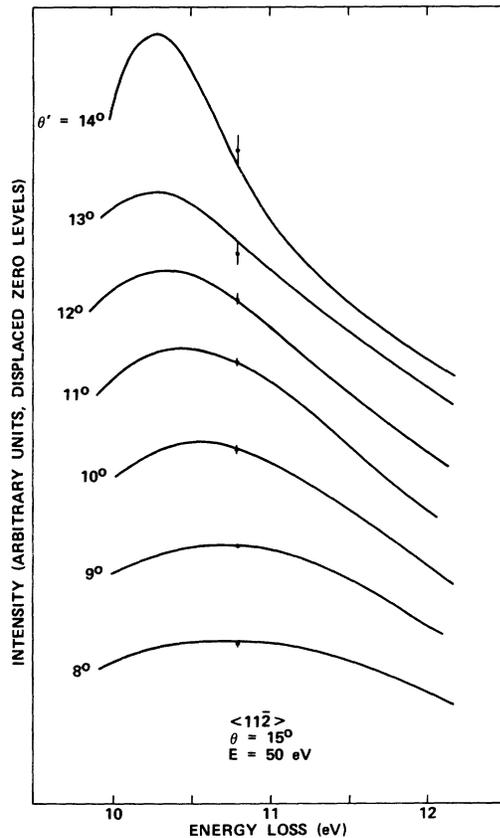
FIG. 14. Fine grid energy-loss profiles correspond-
ing to Fig. 9.

peak shifts to smaller angles with increasing $p_{\parallel}$,
and diminishes in intensity as a result of the dimin-
ishing lifetime. The new peak appearing near the
15° specular direction for $w \geq 12.8$ eV is the prin-
cipal bulk-plasmon peak. A third peak which ap-
pears at lower angles in this range of w apparently
is also associated with the bulk plasmon, but is dy-
namical in origin. In earlier evaluations of the
SPDL the low-angle peak was interpreted as the ex-
tension of the surface-plasmon peak to large values
of w. The earlier interpretation is not supported
by the more extensive loss-profile data now avail-
able. Although a corresponding low-angle peak is
visible in the loss profiles at $\theta' \leq \theta - 10°$, it is
clearly separate from the surface-plasmon com-
ponent, which can be simultaneously identified at
lower values of w.

Since extensive loss-profile data similar to that
reported here for substrate No. 2 is unavailable for
substrate No. 1, angular profiles provide the only
equivalent basis for comparing the two substrates.
Comparisons were made under the following condi-
tions: $\langle 11\bar{2} \rangle$ azimuth; $\theta = 15°$; $E = 50$, 55, 60 eV;
$w = 8.4–18.4$ eV, $\Delta w = 2$ eV; $\theta' = 0°–30°$ $(\Delta\theta' = 2°)$.

In all cases corresponding peaks whose position
agrees to within 1° were found. This is well within
the combined uncertainty of the two sets of data.

D. Surface-Plasmon Dispersion and Lifetime

The SPDL derived from the present data is signif-
icantly different from that previously reported.[10,11]
The principal reason for this is related to the rein-
terpretation of the *angular* profiles, particularly
the disassociation of the dynamical low-angle peak
from the surface plasmon. Confining the analysis
to the *loss* profiles effectively forces this condition
since dynamical influences are largely eliminated.
Since exclusion of the low-angle peak represents a
loss of information at large w, the present results
depend much more heavily on the information avail-
able at small w. The demands on precision in both
data and theory are therefore much greater than
previously realized.

The QFTM analysis of data reported in the pres-
ent work is presented in the following paper. The
SPD most consistent with the available data is
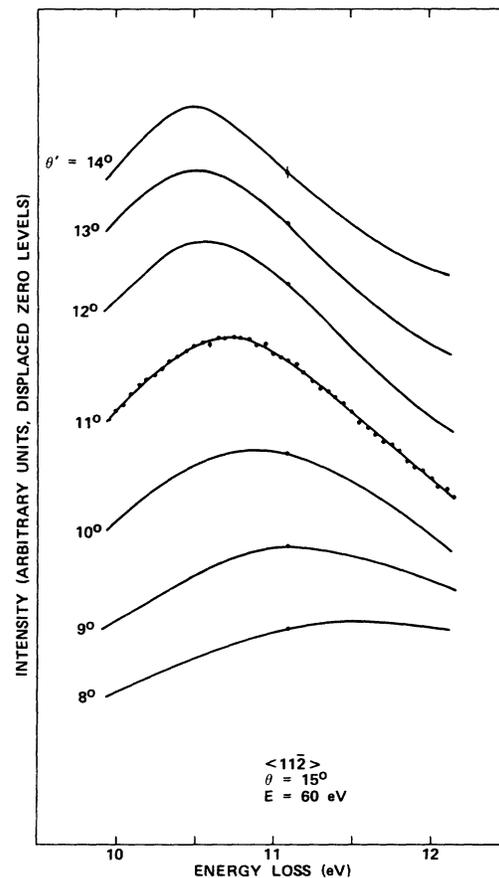
FIG. 15. Fine grid energy-loss profiles correspond-
ing to Fig. 10.

$$\hbar\omega_s = 10.5 \pm 0.1 + (2 \pm 1)p_{\shortparallel} + (0^{+2}_{-0})p_{\shortparallel}^2 ,   \quad (3)$$

where $\hbar\omega_s$ is in eV and $p_{\shortparallel}$ in Å^{-1}. The correspond-
ing lifetime $\hbar/\Gamma_s$, expressed in terms of the damp-
ing Γ_s, is found to be

$$\Gamma_s = 1.85 \pm 0.5 + (3 \pm 2)p_{\shortparallel} ,   \quad (4)$$

where Γ_s is in eV. Comparison with earlier re-
sults shows the SPD given by Eq. (3) to be much
flatter as $p_{\shortparallel}$ increases from zero.[15]

The flatter SPD and internal consistency of the
data are supported by the CLM within its more se-
vere accuracy limitations. Because of the large
Δw grid in the data available for this type of anal-
ysis and the restriction of pertinent information to
small w, the evaluation of $p_{\shortparallel}$ is carried out for $\hbar\omega_s$
= 12 eV only. To maximize accuracy and minimize
the dependence on dynamical peculiarities of the in-
elastic energy profile the following procedure is
used: All loss profiles exhibiting a prominent sur-
face-plasmon LD maximum at $w = 12$ eV are se-
lected from the appropriate set of data. Equation
(10) of Ref. 11 is applied directly to the parameters
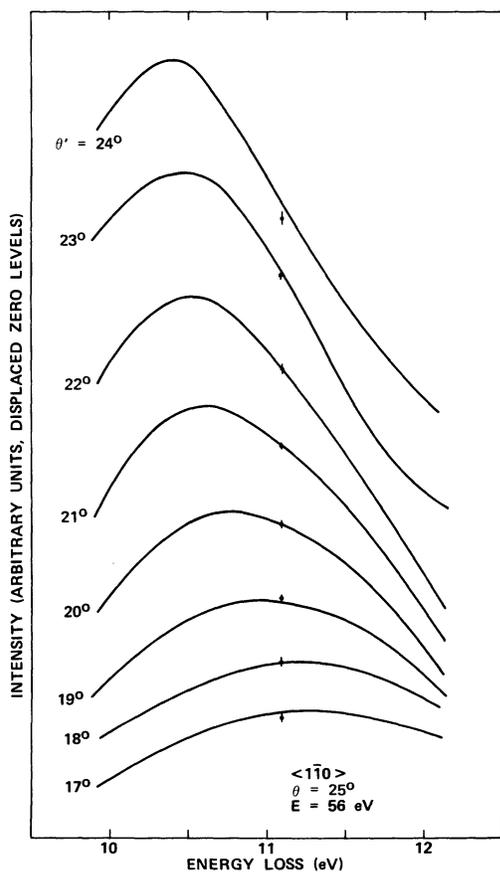
FIG. 16. Fine grid energy-loss profiles correspond-
ing to Fig. 13.
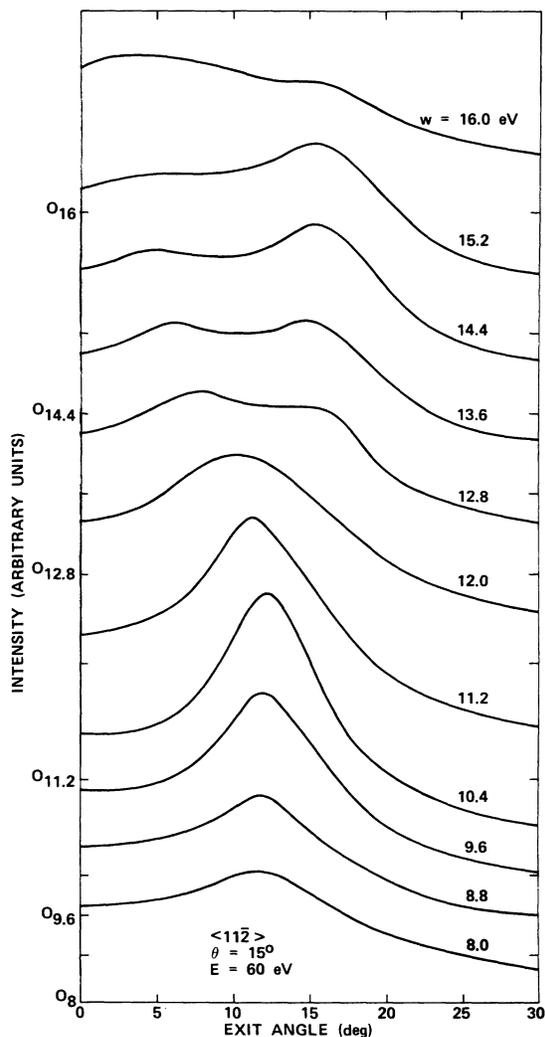
FIG. 17. Coarse grid angular profiles derived from
the loss profiles of Fig. 10. The energy-loss grid has
been increased from 0.4 to 0.8 eV for presentation clari-
ty. The tick marks along the vertical axis indicate
displaced zero levels.

associated with these profiles to obtain $p_{\shortparallel}$ (former-
ly K). Extreme values for each of six available
combinations of E_B and θ are used to define six in-
dividual ranges of admissible $p_{\shortparallel}$ values. Results
are given in Table II. The existence of a range
common to all six of the individual ranges allows
internal consistency within the $\langle 11\bar{2} \rangle$ azimuth. Al-
though the common range does not contain the most
probable QFTM result, it does fall well within the
range of uncertainty. This minor discrepancy is
due in part to the inclusion in the QFTM analysis of
information from the less prominent LD peaks,
which have not been included in the CLM analysis.
These peaks, which occur in the range $\theta' > \theta$ often
indicate a flatter dispersion than the more intense

TABLE II. Comparison of models ($\hbar\omega_s = 12$ eV).

Model	$p_{\parallel}$ range designation	E_B(eV)	θ(deg)	Range min $p_{\parallel}$ (Å^{-1})	Range max $p_{\parallel}$ (Å^{-1})
CLM	individual	49	15	0.55	0.78
CLM	individual	99	15	0.51	0.69
CLM	individual	52	20	0.46	0.59
CLM	individual	106	20	0.53	0.70
CLM	individual	55	25	0.47	0.80
CLM	individual	107	25	0.55	0.73
CLM	over-all			0.46	0.78
CLM	common			0.55	0.59
QFTM	most probable			0.75	
QFTM	uncertainty			0.37	1.6

peaks at $\theta' < \theta$.[15] The neglect of bulk-plasmon over-lap in the CLM may also be significant. In general, the QFTM result represents a much larger body of data, including both DL and LD processes, as well as two azimuths. The CLM results therefore can be expected only to form a subset of the QFTM un-certainty range,[15] which Table II clearly shows to be the case.

An additional consideration in comparing Eqs. (3) and (4) with the previously reported SPDL is the role of surface roughness. It is conceivable that the effect of roughness contouring on the electron-density distribution at the surface has a significant influence on both dispersion and lifetime. Since substrate No. 1 exhibits visible irregularities which were not evident on substrate No. 2, it might be ex-pected that results for the two substrates would be substantially different. Unfortunately, the exten-sive loss-profile data, required to perform an ac-curate analysis on substrate No. 1, is lacking. Since the previously reported analyses[10,11] were largely based on data features now tentatively asso-ciated with the bulk plasmon, this type of result has little relevance to surface roughness. The only per tinent basis for comparison of the two substrates is the surface-plasmon peak in the limited angular profile data previously discussed. From the lack of evidence for any significant discrepancy in the position of this peak, we conclude that the SPD de-termined from ILEED is relatively insensitive to visible long-range irregularities. The SPD may, however, be sensitive to irregularities on a much smaller scale. This can only be determined by fu-

ture experiments on surfaces with carefully con-trolled short-range irregularities.

V. SUMMARY

ILEED measurements near the (00) elastic beam from epitaxial Al(111) have been extended and im-proved, with precise determination of the surface-plasmon dispersion and lifetime as the principal ob-jective. Emphasis has been shifted from angular to loss profiles in view of the latter's predominant ki-nematic property as demonstrated in recent theo-retical work. A smaller data grid and more effi-cient data-collection procedure provides a signifi-cant improvement in signal-to-noise ratio and res-olution. Under favorable conditions the relative position of energy-loss peaks can be located to with-in 50 meV with 2° angular resolution. Measure-ments have been extended to include two different Bragg peaks, two angles of incidence, and two crys-tallographic directions. The analysis has shown these to be largely consistent, yielding internally consistent results for the surface-plasmon disper-sion and lifetime. These results differ from those previously reported on the basis of more limited and less precise data. The difference is mainly at-tributable to an enlightened interpretation of the new data resulting from new theoretical results. The use of a visibly smoother substrate evidently has little influence, although sensitivity to short-range roughness cannot be excluded on the basis of present work. Further ILEED measurements on surfaces with controlled irregularities on a lateral scale of 100 Å or less are needed to explore this. Measurements on other crystallographic faces and an investigation of the influence of chemisorbed layers on the SPDL would also be of considerable interest.

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Surface-Plasmon Dispersion in Al(111) Films

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The extraction of the surface-plasmon dispersion relation from experimentally measured inelastic low-energy- $(20 \lesssim E \lesssim 200$ eV) electron diffraction intensties on Al(111) films is described. Our analysis is based on the two-step model of inelastic diffraction. Attention is focused on the methodology of determining the model parameters from the data analyses, the internal consistency of parameters obtained from the consideration of independent data, and the accuracy of the values of the parameters as determined using our procedure. Examination of eight independent sets of experimental intensities leads to the dispersion relation $\hbar \omega_s(p_{||}) = 10.5(\pm 0.1) + 2(\pm 1)p_{||} + 0 \ (+2)p_{||}^2$; $\Gamma_s(p_{||}) = 1.85(\pm 0.5) + 3(\pm 2)p_{||}$, for energies measured in eV and momenta in Å^{-1}.

I. INTRODUCTION

The principal thrust of modern surface spectroscopy is the determination of the chemical, geometrical, vibrational, and electronic structure of the upper few layers of a solid in a high-vacuum environment.[1] The three major techniques for determining those features of the electronic excitation spectra associated with solid surfaces are inelastic low-energy-electron diffraction (ILEED), ion-neutralization spectroscopy (INS), and photoelectron spectroscopy (PES). In a previous paper[2] we constructed a procedure for analyzing ILEED intensity data to extract from them the dispersion relation of electronic surface excitations. Herein we apply this procedure to determine, from data taken by Porteus and Faith,[3] the dispersion relation of surface plasmons[4] at the vacuum interface of Al(111). Our results,

$$\hbar \omega_s(p_{||}) = 10.5(\pm 0.1) + 2(\pm 1)p_{||} + 0(+2)p_{||}^2, \quad (1a)$$

$$\Gamma_s(p_{||}) = 1.85(\pm 1) + 3(\pm 2)p_{||}, \quad (1b)$$

already have been reported.[5] In Eqs. (1) $\hbar \omega_s(p_{||})$ is the real part of the energy of the surface plasmon measured in eV as a function of its wave number $\vec{p}_{||}$ for motion parallel to the surface measured in Å^{-1}. The quantity $\Gamma_s(p_{||})$, also measured in eV, is the imaginary part of this energy, which provides a measure of the lifetime of the surface plasmon. These results supersede those based on an earlier study by Bagchi and Duke[6] of a more limited range of data. In this paper we describe the analysis from which Eqs. (1) were obtained and compare it with the previous one.[6] We proceed in two steps. First, in Sec. II we review the definition[2] of our analytical procedure, and dispense with a few preliminary items such as the selection of data and the distinction between inelastically *diffracted* beams and the incoherent background on which they are superposed. Then, in Sec. III we describe our analysis of the selected ILEED intensities. We conclude our presentation with a brief synopsis in Sec. IV.