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Characteristic Energy-Loss Spectra and $-\mathrm{Im}(1/\epsilon)$ for Amorphous and Polycrystalline Al_2O_3†

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Characteristic energy-loss spectra of 20-keV electrons in amorphous and polycrystalline Al_2O_3 have been measured in transmission at zero scattering angle. The dominant loss peak, due to plasmon excitation, occurred at 22.6±0.2 and 24.3±0.2 eV for the amorphous and polycrystalline films, respectively. Lower-lying weaker losses were observed at about 8.7 and 13.5 eV in both films, with an additional loss at 17.7 eV in the polycrystalline film. Using a previously developed technique, values of $-\mathrm{Im}\epsilon^{-1}$ and electron-energy-loss oscillator strength were derived from the loss spectra. The results for anodized Al_2O_3 are in excellent agreement with existing optical measurements.

THE dependence of characteristic energy-loss spectra on amorphous and polycrystalline structure has been measured for only a few materials, such as C,[1] Si,[2] Ge,[2,3] and As.[3] The dominant loss peak of at least the first three of these materials is due to a collective electron excitation, or plasmon, and the difference in position of this peak in the crystalline and amorphous forms is interpreted as a density effect, the loss peak for the lower-density amorphous specimen occurring at a lower energy. The dominant ≈23-eV loss peak in Al_2O_3 is also due to a collective electron excitation since recent optical measurements by Freeman[4] on anodized Al_2O_3 and Stephan, Lemmonier, and Robin[5] on α-Al_2O_3 show a peak in $-\mathrm{Im}(1/\epsilon)$ at ≈23 eV where both the real and imaginary parts of the dielectric constant $\epsilon=\epsilon_1+i\epsilon_2$ are small.[6]

Previously, Swanson and Powell had found a difference between amorphous and polycrystalline Al_2O_3 electron-energy-loss spectra in the 75–90-eV loss region corresponding to Al L-shell excitation.[7] The energy-loss measurements described here on these films in the 0–40 eV range also showed a structure dependence. Values of $-\mathrm{Im}(1/\epsilon)$ over this energy range for the two forms of Al_2O_3 were derived from the energy-loss spectra by a comparison technique using an Al specimen (of known cross section) and the relation between $-\mathrm{Im}(1/\epsilon)$ and the oscillator strength for electron energy loss. The total scattering cross section for 20-keV electrons was also calculated for both materials. The values obtained for $-\mathrm{Im}(1/\epsilon)$ for anodized Al_2O_3 were in excellent agreement with the results of optical measurements.

1. EXPERIMENTAL

The characteristic energy-loss spectra were measured in transmission through thin-film specimens at 20-keV primary energy and zero scattering angle, using an energy analyzer with a resolution of about 1 eV.[8] The angular spread of the primary beam is typically 1.6 mrad full angular width at half-maximum, and the analyzer has an acceptance half-angle of about 0.25 mrad.

Amorphous Al_2O_3 films were prepared by anodization of Al foil[9] while polycrystalline γ-Al_2O_3 films were prepared by heating evaporated Al films in air at ≈700°C for 7 h.[7,10] The film thicknesses were 15.5±1.0 $\mu g/cm^2$ for the γ-Al_2O_3 films and 13.6±1.4 $\mu g/cm^2$ for the anodized films. These film thicknesses were determined by weighing a known area of an anodized film and by assuming complete oxidation of an 8.2-$\mu g/cm^2$ Al film whose thickness had been monitored during evaporation by a quartz-crystal microbalance. The respective film densities were 2.8 g/cm^3 using a film thickness of 13.0 Å/V from the anodization process[10] and 3.7 g/cm^3 using an average value for γ-Al_2O_3.[11] These densities indicate thicknesses of 490 and 420 Å for the anodized and γ-Al_2O_3 films, respectively. The positions determined for the energy-loss maxima (Table I) were based on measurements taken on three anodized and two γ-Al_2O_3 films. The values of $-\mathrm{Im}(1/\epsilon)$ were derived from loss spectra on one film of each type.

2. RESULTS

Typical loss spectra are shown in Fig. 1 for the polycrystalline γ-Al_2O_3 films (Curve A) and the amorphous, anodized films (Curve B). Weaker loss peaks are superimposed on the low-energy side of the dominant plasmon loss, two for the anodized specimen and three for the γ-Al_2O_3 specimen. The estimated locations of these peak maxima[12] are marked with vertical lines in the figure,

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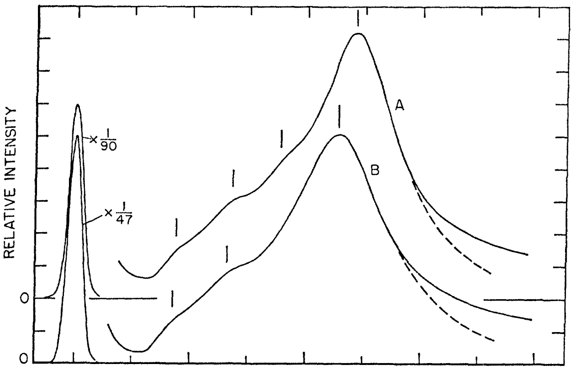

FIG. 1. Energy-loss spectra of γ-Al_2O_3 (curve A) and anodized Al_2O_3 (curve B). Maxima in the loss spectra are marked by vertical lines. The dashed line represents the intensity attributed to the dominant loss peak.

and are tabulated in Table I. (The second multiple of the plasmon loss could be seen as a very weak peak beyond 40 eV, not shown in the figure.) There is a distinct difference, almost 2 eV, between the positions of the plasmon loss peaks in the two specimens.

The expected positions of the two plasmon losses, assuming a purely free-electron model for 24 valence electrons per molecule,[13] can be calculated from[6]

$$\hbar\omega_e \approx \hbar\omega_p[1-(1/8\omega_p^2\tau^2)],$$

where $\omega_p=(4\pi ne^2/m)^{1/2}$ is the free-electron plasma frequency and τ is the relaxation time. Here e and m have their conventional meaning, while n is the valence-electron density and $\hbar/\tau$ is approximately the loss-peak full width at half-maximum (FWHM).[14] On this model, $\hbar\omega_e=23.0$ and 26.5 eV for the anodized and γ-Al_2O_3 specimens, respectively, compared to the respective measured peak positions at 22.6±0.2 and 24.3±0.2 eV. (The plasmon loss was assumed to be symmetrical,[14] with a FWHM of twice the width from the peak maximum to the half-maximum intensity on the high-energy-loss side. The remaining peak width was attributed to the lower-lying losses.) Although the plasmon energy-loss positions seem to be well represented by this model, the dielectric constant differs considerably from a free-electron dielectric constant over a substantial portion of the measured energy range.[4,5]

TABLE I. Maxima in the characteristic energy-loss spectra of anodized Al_2O_3 and γ-Al_2O_3 together with the maximum in $-\text{Im}\epsilon^{-1}$ from Freeman's optical measurements on anodized Al_2O_3. The quoted errors for the anodized Al_2O_3 are the standard deviation of nine measurements, and for the γ-Al_2O_3 are estimates based on five measurements. The corresponding maxima in the derived $-\text{Im}\epsilon^{-1}$ occur about 0.4 eV higher in energy.

γ-Al_2O_3 (eV)	Anodized Al_2O_3 (eV)	Anodized Al_2O_3 (optical) (eV)
8.7±0.4	8.6±0.2	
14.0±0.4	13.2±0.3	
17.7±0.4	...	
24.3±0.2	22.6±0.2	23.3

The differential scattering cross section per electron of the solid for an energy loss E and momentum transfer q from the primary electron to the solid is given by

$$\frac{d^2\sigma}{dEdq}=\frac{2\pi e^4}{E_0E}\frac{f_E(q)}{q}, \tag{1}$$

where E_0 is the primary energy and $f_E(q)$ is the generalized oscillator strength for the scattering process[15–17] normalized to $\int_0^\infty f_E dE=1$. (References 15 and 16 apply to atoms and Ref. 17 discusses the generalization to solids.) The angular dependence of the differential cross section varies with energy loss E through the dependence of momentum transfer q on scattering angle θ: $q=(2mE_0)^{1/2}(\theta^2+\theta_E^2)^{1/2}$, where $\theta_E=E/2E_0$. The energy-loss spectrum observed at nominally zero angle represents the folding of the differential cross section with the primary-beam angular distribution integrated out to the acceptance angle of the energy analyzer. The energy analyzer accepts all electrons scattered within a fixed angular cone of acceptance for all energy losses, and hence a larger fraction of the scattered electrons is detected for small energy loss than for large energy loss. Consequently, the measured energy-loss spectrum is not proportional to the differential cross section. A correction factor, which increases with energy loss in a manner depending on the primary beam-analyzer geometry, must be used to multiply the observed loss intensity at nominally zero angle to give the differential cross section.[17,18]

If the angular characteristics of the primary beam and energy analyzer are known, the differential cross section and oscillator strength $f_E(q)$ for a q corresponding to $\theta=0$ can be calculated. At $\theta=0$, $q=q_{\min}=(mE^2/2E_0)^{1/2}$. The procedure for obtaining $f_E(q_{\min})$ from a characteristic loss spectrum has been described previously.[17] In this procedure, a comparison standard film of Al, whose cross section is known, is used to eliminate the need for an exact knowledge of the angular characteristics of the apparatus.

For $E_0 \gg E$, $f_E(q_{\min})\approx f_E(0)$, the oscillator strength for zero momentum transfer.[15] A sum rule for $-\text{Im}[1/\epsilon(E,q)]$ can then be applied to obtain the

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[18] H. Raether, Ergeb. Exakt. Naturw. **38**, 125 (1965); M. Creuzburg, Z. Physik **196**, 433 (1966).

$-\mathrm{Im}[1/\epsilon(E,0)]$ corresponding to optical processes[19]:

$$\int_0^{E_1} E\,\mathrm{Im}[\epsilon(E,0)]^{-1}dE=-\tfrac{1}{2}\pi\hbar^2\frac{4\pi Ne^2}{m}Zg(0)\,, \tag{2}$$

where N is the number of molecules per unit volume, Z is the total number of electrons per molecule, and $g(0)$ is the integrated oscillator strength for energy-loss processes between $E=0$ and $E=E_1$. Differentiating Eq. (2) yields[20]

$$-\mathrm{Im}\epsilon^{-1}=\frac{2\pi^2\hbar^2Ne^2}{mE}Zf_E(0)\,. \tag{3}$$

The primary-beam angular distribution and the zero-angle loss spectrum of an Al and an Al_2O_3 film were recorded in succession. Using 360 Å as the mean free path for plasmon excitation in Al at 20 keV,[17] values of f_E were calculated from the Al_2O_3-loss spectra at 1-eV intervals. The corresponding results for $-\mathrm{Im}\epsilon^{-1}$ are shown in Fig. 2 for the anodized Al_2O_3 and γ-Al_2O_3. The integrated oscillator strengths $g(0)$ for the 6–35-eV region are listed in Table II.

To calculate the scattering cross section $d\sigma/dE$ for energy loss E integrated over angle, the oscillator strength $f_E(q_{\min})$ was assumed to be constant over an angular range of integration corresponding to $q_{\min}\leq q\leq q_{\max}=(2mE)^{1/2}$ for each incremental E.[16,17] Then

$$\frac{d\sigma}{dE}=\frac{\pi e^4f_E(0)}{E_0E}\ln\left(\frac{4E_0}{E}\right). \tag{4}$$

This choice of $q_{\max}$ overestimates the angular range of a free-electron plasmon loss.[17] However, since there is a considerable contribution to the loss spectrum from single-electron excitations at the lower-energy losses, and since $q_{\max}$ affects $d\sigma/dE$ only logarithmically, this choice of $q_{\max}$ is believed to be reasonable considering the over-all accuracy of the measurements. The results for the total scattering cross section σ_t for the 6–35-eV region are summarized in Table II.

The precision of these measurements for $f_E(0)$, σ_t, and $-\mathrm{Im}(1/\epsilon)$ is estimated to be ±20%, while the accuracy, including the uncertainty in the Al mean free path and in the assumption that there is no background continuum under the energy-loss spectra, is estimated to be ±35%, adding the various uncertainties quadratically. There is an additional inaccuracy in σ_t due to the choice of $q_{\max}$ and the approximation that $f_E(q)=f_E(q_{\min})$ over the range of integration. The values of $f_E(0)$ and σ_t depend on the specimen mass thickness, so that any uncertainty in the density only affects $-\mathrm{Im}(1/\epsilon)$ [through N in Eqs. (2) and (3)].

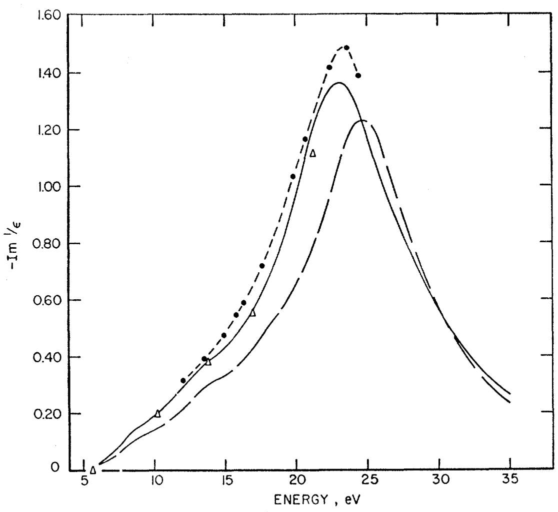

FIG. 2. A plot of $-\mathrm{Im}\epsilon^{-1}$ derived here for anodized Al_2O_3 (solid line), and γ-Al_2O_3 (long-dashed line). The maxima in $-\mathrm{Im}\epsilon^{-1}$ occur about 0.4 eV higher than the corresponding maxima in the loss spectra tabulated in Table I. For comparison the results of Freeman (dot-dash line) and Hass and co-workers (Δ) for optical measurements on anodized Al_2O_3 are included.

Since the results for σ_t and $g(0)$ for the anodized and γ-Al_2O_3 specimens differ by an amount just within the combined precisions of the measurements, their differences are not necessarily significant.

3. DISCUSSION

Numerous measurements have been made previously of the characteristic loss spectrum of Al_2O_3,[21–25] but no differences between the two forms of Al_2O_3 have been reported. Differences between anodized and γ-Al_2O_3 energy-loss spectra corresponding to differences seen in the L-shell x-ray absorption spectra in the 75–90-eV region[26] have been observed by Swanson and Powell.[7]

TABLE II. Values obtained for the integrated oscillator strength $g(0)$ and total cross section per electron σ_t for electron scattering with energy loss between 6 and 35 eV in Al_2O_3 at 20 keV. $Z(=50)$ is the number of electrons per molecule. The precision and accuracy of $g(0)$ is estimated to be ±20 and ±35%, respectively. The precision of σ_t is the same as that of $g(0)$, with some additional inaccuracy due to the angular integration (see Sec. 2). The difference in the results for the two kinds of Al_2O_3 is therefore not necessarily significant.

	γ-Al_2O_3 $\times10^{-19}$	Anodized Al_2O_3 $\times10^{-19}$
$\sigma_t(\mathrm{cm}^2)$	1.7	2.6
$g(0)$	0.15	0.22
$Zg(0)$	7.6	11

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Measurements of the optical constants of anodized Al_2O_3 have been made by Freeman in the energy range from 12 to 24 eV at intervals of about 1 eV,[4] and by Hass and co-workers at five energies between 5 and 22 eV.[27] Values of $-\mathrm{Im}(1/\epsilon)$ calculated from their results are plotted in Fig. 2. Optical constants of α-Al_2O_3 (corundum) measured between 9 and 40 eV by Stephan, Lemonnier, and Robin[5] give a maximum in $-\mathrm{Im}(1/\epsilon)$ at about 23 eV and a subsidiary peak at 16 eV.

The results obtained here for $-\mathrm{Im}(1/\epsilon)$ for anodized Al_2O_3, shown in Fig. 2, are in excellent agreement with the two previous optical measurements. The displacement in energy of the curve of $-\mathrm{Im}(1/\epsilon)$ for γ-Al_2O_3 with respect to that of anodized Al_2O_3 is significant, though the magnitude of $-\mathrm{Im}(1/\epsilon)$ is not known to better than 35% in each case.

At energy losses above about 30 eV, the contribution of the second-multiple-loss intensity to the tail of the dominant first-loss peak becomes significant. To allow for this contribution, the values for $-\mathrm{Im}(1/\epsilon)$ were extrapolated to 35 eV by assuming a Lorentzian line shape fitted to the peak maximum and upper half-width at half-maximum. The corresponding loss intensity attributed to the dominant loss peak is shown as a dashed line in Fig. 1.

A recent optical-absorption measurement on anodized Al_2O_3 [28] shows the absorption edge occurring at about 7 eV, with a shoulder near the energy-loss maximum at 8.6 eV. The energy-loss peak at about 13.5 eV is probably due to another optical-absorption maximum, although Freeman's rather widely spaced data points show no indication of a subsidiary peak in either ϵ_2 or $-\mathrm{Im}(1/\epsilon)$ near this energy. The energy loss at 8.7 eV in γ-Al_2O_3 seems to correspond to optical absorption in α-Al_2O_3, which rises very rapidly from 8.3 to 9.5 eV.[5] The energy-loss peak at 17.7 eV in γ-Al_2O_3 may be related to the peak in $-\mathrm{Im}(1/\epsilon)$ at 16 eV seen in α-Al_2O_3. The broader width found for the plasmon loss of the anodized specimen (10.2 eV) compared to that of the γ-Al_2O_3 specimen (8.9 eV) agrees with the observation of Zeppenfeld and Raether for plasmon-loss peaks in amorphous and polycrystalline Ge and Si.[2]

Less than one-half of the 24 valence electrons are participating in the energy-loss process in Al_2O_3 out to an energy loss of 35 eV. [From Eq. (3) and the results in Fig. 2, it is clear that the electron oscillator strengths calculated from the optical results will closely approximate our $f_E(0)$.] Since there are no strong electron-energy-loss peaks between 35 eV and the Al L_{23} edge, the remaining oscillator strength presumably occurs as an absorption continuum at energies beyond 35 eV.[29] Since Al_2O_3 infrared absorption begins at energies below ≈ 0.19 eV,[30] it is unlikely that there will be significant oscillator strength in this region.

4. CONCLUSIONS

Distinct differences in the characteristic loss spectra of (amorphous) anodized Al_2O_3 and (polycrystalline) γ-Al_2O_3 have been observed. Both the position and linewidth of the dominant energy loss differ in the two materials, with the lower-density amorphous Al_2O_3 showing the expected lower energy loss and broader linewidth. Values of $-\mathrm{Im}(1/\epsilon)$ and oscillator strength $f_E(0)$ for electron energy loss have been calculated from the loss spectra in the 6–35-eV energy range and are in excellent agreement with available optical measurements. The results for $f_E(0)$ show that less than one-half of the 24 valence electrons are participating in the energy-loss process in the measured energy-loss range.

ACKNOWLEDGMENTS

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