Infrared optical properties of evaporated alumina films

T. S. Eriksson, A. Hjortsberg, G. A. Niklasson, and C. G. Granqvist

The dielectric function $\epsilon \equiv \epsilon_1 + i\epsilon_2$ has been determined for Al_2O_3 films prepared by electron beam evaporation, in the 5–50-μm wavelength range. The data were extracted from spectrophotometric recordings of transmittance and reflectance by use of a novel technique. Supplementary measurements were made of the refractive index for visible and near-infrared wavelengths and of the dielectric constant at 1 MHz. Kramers-Kronig analysis was employed to check the consistency of our results for ϵ_1 and ϵ_2.

I. Introduction

We investigate the optical properties of electron beam evaporated aluminum oxide in the 0.3–50-μm wavelength range. The complex dielectric function is evaluated from spectrophotometric data by use of a novel accurate technique.[1]

Films comprised of compact aluminum oxide can be prepared by many techniques such as vacuum evaporation of Al_2O_3, sputtering, chemical vapor deposition, anodization to form barrier-type coatings, and controlled oxidation of Al. These compact Al_2O_3 coatings show a combination of many favorable properties: they are excellent dielectrics with good adherence to most substrates, their hardness as well as abrasion and scratch resistance is very large, they are corrosion resistant and withstand high temperatures and energetic radiation. Porous alumina coatings, with somewhat less ideal characteristics, are applied as a surface treatment of aluminum by conventional anodizing on a very large industrial scale. The superior properties of Al_2O_3 and the established preparation techniques have led to a widespread use of such coatings in several fields. We particularly note the applications to spectrally selective surfaces for efficient photothermal conversion of solar energy,[2,3] in which Al_2O_3 is used in multilayer interference stacks[4] and in cermet films.[5–7] A detailed theoretical understanding of these and other[8] types of spectrally selective surface requires knowledge of the dielectric function of Al_2O_3 throughout the thermal infrared range. Such data have been available for anodic alumina films[9,10] and crystalline material[11–15] (corundum, sapphire, ruby) for many years, whereas no previous determination seems to have been published for evaporated Al_2O_3 in spite of its great technological importance.

In Sec. II below we discuss the technique to fabricate the Al_2O_3 layers by vacuum evaporation using electron beam heating. The films were characterized by determinations of the refractive index for visible and near-infrared light; our results agree with previous data[16] for similarly produced films. Section III presents spectrophotometric recordings of infrared transmittance and reflectance. These results are used in Sec. IV to provide an accurate determination of the complex dielectric function. As discussed in Sec. V, our data are fully consistent with the Kramers-Kronig relations. Throughout the paper we make comparisons between the properties of alumina films prepared by different techniques.

II. Alumina Films

Films were prepared by evaporation of Al_2O_3 pellets (Materials Research Corp.) with a stated purity of 99.992%, from an 8-kW electron beam source mounted in an oil diffusion pumped stainless steel chamber. The residual pressure was ~0.6 mPa prior to deposition, the main constituent being water vapor. During the deposition the pressure rose to ~2.7 mPa. The evaporation rate was typically 0.7 nm/sec, as read on a quartz crystal oscillator microbalance. The Al_2O_3 vapor was condensed onto substrates placed 55 cm above the source; we used plates of KRS-5 (thallium-bromide-iodide), crystalline Si, and Corning 7059 glass with and without a predeposited opaque coating of resistively evaporated Al. During the Al_2O_3 deposition the substrate temperature rose to $\gtrsim$50°C.

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Electron beam diffraction analysis yielded very diffuse rings whose diameters seemed to be consistent with a basic atomic arrangement of the γ-Al_2O_3 type. In this respect, it appears that the evaporated Al_2O_3 films resemble those made by anodization.[17] X-ray studies of the Al_2O_3 films yielded no observable structure in the diffraction pattern.

Film thicknesses were determined by optical interference in the visible and near-infrared spectral ranges. These readings were checked against data taken with an Alpha-Step mechanical stylus instrument. The accuracy in our thickness measurements is estimated to be ±3%.

We investigated more than 30 Al_2O_3 films with thicknesses from 0.3 to 3.6 μm. The latter value represents a practical upper limit, and attempts to make even thicker layers always resulted in a partial or complete disintegration which presumably was caused by excessive interfacial stresses.

Alumina films prepared by electron beam evaporation are not necessarily stoichiometric, since the evaporant can be partially decomposed thermally as well as by the electron bombardment. Direct evidence for such a dissociation was gained in a mass spectroscopic analysis[18] of evaporation products, which clearly showed the presence of free oxygen. It is also known[19] that improper deposition conditions can give spurious optical absorption. Hence it is of prime importance to assess the reproducibility of the optical data both between films prepared during different runs and between the present data and those of previous investigations. The internal consistency of our results was found to be excellent, and different films showed virtually identical optical characteristics. The agreement with earlier published results was verified primarily by comparison of refractive indices in the visible and near-infrared spectral ranges as discussed below. Additional support was gained from comparison of infrared reflectance spectra; these will be treated later.

Figure 1 shows the refractive index for different kinds of alumina in the $0.35 < \lambda < 2.1$-μm range, where the material is nonabsorbing. The solid curve represents an evaluation based on reflectance and transmittance determinations for three of our films deposited onto glass. These measurements were taken with a Beckman ACTA MVII double-beam spectrophotometer. The absolute accuracy is believed to be ±0.02. These data agree well with the dashed curves reproduced from a study of electron beam evaporated Al_2O_3 by Cox *et al.*[16]; the lower dashed curve pertains to a substrate temperature of 40°C and the upper dashed curve to 300°C. Similar results for the refractive index of vapor-deposited Al_2O_3 have been reported elsewhere.[20–24] In our case, the substrate temperature lay between the extremes of Cox's work, which is fully consistent with the solid curve falling in between the dashed ones. For comparison, the dash–dot curve shows data for bulk sapphire as taken from Malitson *et al.*[25] The refractive index is seen to be larger for crystalline sapphire than for disordered and less dense vapor-deposited films, which is the expected result.

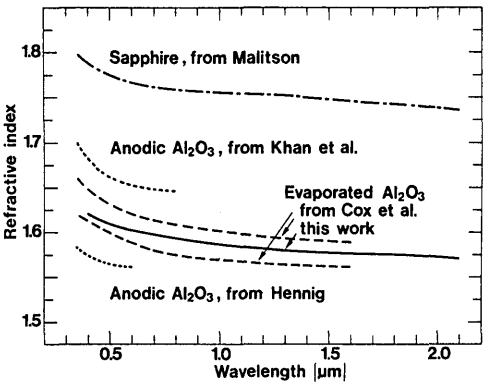


Fig. 1. Wavelength-dependent refractive index of Al_2O_3. Solid curve denotes the present data, dashed curves are reproduced from Ref. 16, dash–dot curve is taken from Ref. 25 (ordinary ray, 24°C), and dotted curves pertain to barrier-type anodic films prepared in ammonium citrate (lower curve, from Ref. 26) and in ammonium borate (upper curve, from Ref. 27).

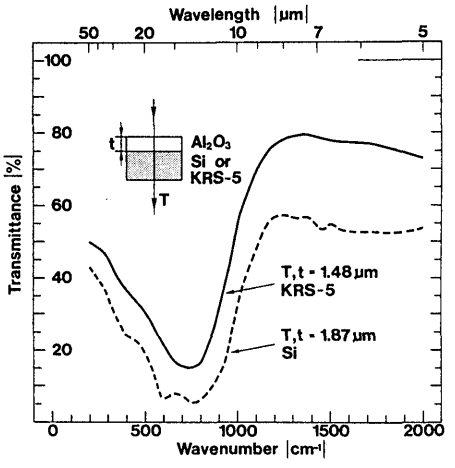


Fig. 2. Spectral transmittance of two Al_2O_3 layers with different thicknesses t deposited onto substrates KRS-5 and crystalline Si.

The dotted curves, finally, denote results from works on barrier-type anodic Al_2O_3 by Hennig[26] and by Khan *et al.*[27] Evidently anodization in different conditions produces films with rather different properties. Similar discrepancies can be found among other works on anodization of Al.[24,28–33]

III. Infrared Spectra

Infrared spectra were recorded in the $2.5 < \lambda < 50$-μm wavelength range with a Perkin-Elmer 580B double-beam spectrophotometer equipped with a wire-grid polarizer in common beam position and variable-angle reflectance attachments. An evaporated gold mirror was used as reference in the reflectance determinations.

Figure 2 shows transmittance spectra for normal incidence onto two Al_2O_3 films with different thicknesses deposited onto different substrate materials. The low transmittance in the $300 \lesssim \tilde{\nu} \lesssim 1000$-$cm^{-1}$ frequency

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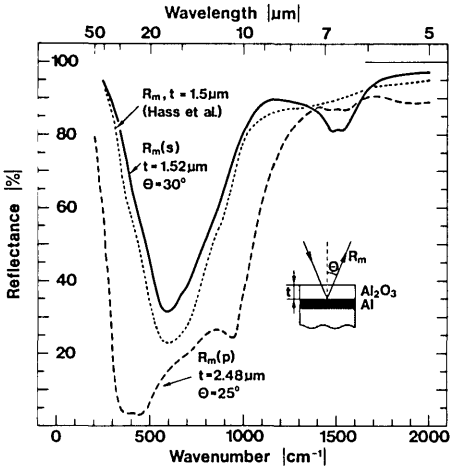


Fig. 3. Spectral reflectance of Al_2O_3 + Al layers with the configuration sketched in the inset. The main figure depicts data for Al_2O_3 films with different thicknesses t, incidence angles θ, and polarizations s and p. The dotted curve is replotted from Ref. 34.

region indicates strong absorption in this range. The tiny structure at 1450 cm^{-1} in the dashed curve stems from absorption in the Si substrate.

Figure 3 depicts a number of infrared reflectance spectra for electron beam evaporated Al_2O_3 deposited onto evaporated Al films backed by very flat and smooth substrates. The solid and dashed curves refer to our measurements with s- and p-polarized light with different incidence angles onto alumina layers with different thicknesses. The most notable feature is the minimum at $300 \lesssim \tilde{\nu} \lesssim 1000$ cm^{-1}, which again indicates strong absorption in this range. Similar data have been published for both evaporated films[21,34,35] and anodized layers.[9,10,36–41]

The solid curve in Fig. 3 can be directly compared with a published spectrum (dotted curve), taken from a work by Hass *et al.*[34] for near-normal incidence onto a similarly prepared sample with almost the same thickness of the Al_2O_3 layer. The two curves are seen to be in overall agreement, which further supports our view concerning the good reproducibility of the properties of electron beam evaporated Al_2O_3. The only significant discrepancy between the two sets of data is the small split valley at $\nu \approx 1500$ cm^{-1} in our measurements. This absorption comes out strongly at the 1.52-μm thickness but is less apparent in the 2.48-μm film since antireflection occurs close to the frequency of the absorption only for the thinner of the films. We believe that this absorption is caused by O—H radicals, but a definite assignment was not attempted. This difference with Hass's result[34] may be a consequence of somewhat different conditions during the film deposition.

In a separate experiment we evaporated Al_2O_3 in the presence of 15 mPa of water vapor. The main effect on the infrared spectra was to induce an absorption peak at ~3000 cm^{-1} and another, less prominent one, at 1650 cm^{-1}. Only small traces of the strongest peak remained in Al_2O_3 films prepared in good vacuum.

IV. Dielectric Function

The complex dielectric function $\epsilon \equiv \epsilon_1 + i\epsilon_2$ was derived from the measured transmittance and reflectance data by computations based on Fresnel's equations.[42] This evaluation employed spectra of the kind shown in Figs. 2 and 3 together with corresponding results for uncoated substrates. Effects of multiple reflections as well as residual absorption in the substrate were included.

In principle any combination of two measurements of transmittance and/or reflectance can be used to determine the dielectric function. However, only certain combinations of data are convenient for extracting this information. The standard practice, involving normal transmittance and near-normal reflectance of a film on an infrared transparent substrate, is awkward for absorbing films[1] since it can give very large errors in the evaluation or physically nonacceptable solutions of Fresnel's equations or possibly no solution at all. Therefore, one of us earlier[1] developed a technique which combines normal transmittance (T) with near-normal reflectance (R_m) of a similar film deposited onto a highly reflecting backing. This (T,R_m) technique is notable for the possibility of yielding reliable values of the complex dielectric function provided the film thickness is properly chosen; it was successfully applied to evaporated silicon monoxide in an earlier paper of ours.[43]

Figure 4 shows data for the real and imaginary parts of the dielectric function for electron beam evaporated Al_2O_3. The solid lines, which were drawn smoothly through a large number of individual points, represent our evaluations based on the (T,R_m) technique using measurements on films with several different thicknesses and with different polarizations of the incident light. The results for ϵ_2 indicate that measurable absorption occurs for $\nu \lesssim 1500$ cm^{-1}. A large absorption peak lies at 630 cm^{-1} and another less pronounced one at 380 cm^{-1}. The ϵ_1 data continue to increase for $\tilde{\nu} >$ 2000 cm^{-1} and join smoothly to the solid curve in Fig. 1.

The shaded areas in Fig. 4 denote the ensuing uncertainties in the magnitudes of ϵ_1 and ϵ_2 caused by a conservatively estimated error of ± 0.01 in the determination of transmittance and reflectance.[1] Possible errors from thickness uncertainties were not included. The evaluated data points for ϵ_1 and ϵ_2 were found to lie well inside the shaded regions. It is seen that the errors are quite small over the main part of the spectral range but increase somewhat at the low frequency end. This increase was difficult to avoid, owing to the earlier noted disintegration of very thick Al_2O_3 films.

V. Analysis and Discussion

The internal consistency in our data for ϵ_1 and ϵ_2 was proved by application of the Kramers-Kronig relation, which can be expressed as

$$\epsilon_1(\omega) = C + \frac{2}{\pi} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'.$$

Here C is the high frequency real dielectric constant.

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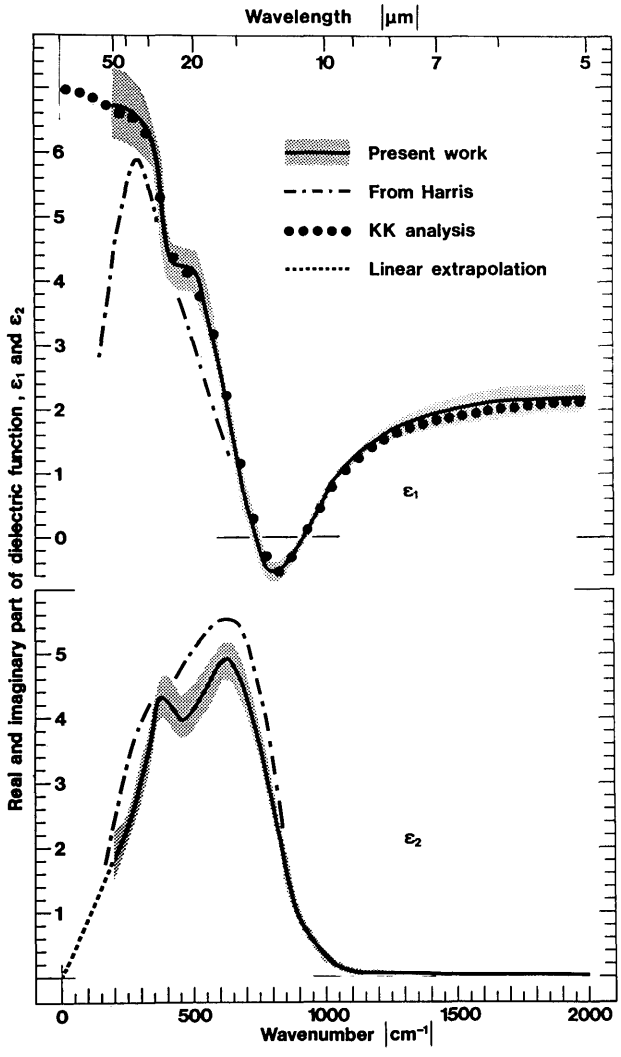


Fig. 4. Real and imaginary parts of the dielectric function for Al_2O_3 films. Solid curves denote our determination, which is accurate to within the shaded areas. Filled circles in the upper part show results for ϵ_1 obtained from a Kramers-Kronig (KK) analysis of the measured ϵ_2 data together with the extrapolation indicated by the dotted line in the lower part of the figure. Dash–dot curves are taken from Harris (Refs. 9 and 10). His error bars become so large for the lowest frequencies that it is doubtful whether the data are meaningful below $\sim 250\ cm^{-1}$.

We set $C = 2.4$, which is consistent with the measured near-infrared refractive index, as seen from Fig. 1. For $\tilde{\nu} < 200\ cm^{-1}$, where no measurements were taken, we assumed a linear extrapolation of $\epsilon_2(\omega)$ toward zero frequency. Such a dependency is expected to hold[44,45] at sufficiently low frequencies in a disordered material. The filled circles in Fig. 4 denote computed data for $\epsilon_1(\omega)$. These are seen to be in excellent correspondence with those directly obtained via the (T,R_m) technique.

In the static limit we find $\epsilon_1(0) = 7.0$ from the Kramers-Kronig analysis. To provide an experimental check on this result, we performed capacitance determinations at 1 MHz and 1 kHz on Al_2O_3 films sandwiched between metal layers. Measurements on several films gave values between 8 and 8.5. The radio-frequency data are thus slightly higher than the extrapolated Kramers-Kronig result, which is not unexpected since some very low frequency absorption caused by water contamination in the films is likely. Our findings for the static dielectric constant are consistent with results from several studies[18,21–23,46,47] of vapor-deposited Al_2O_3 in which this quantity lay between 7 and 9. In a few papers[20,48] somewhat lower values have been stated. Results similar to ours have been given also for Al_2O_3 films prepared by anodization[29,30,33,49] and by other techniques.[50–53] Bulk sapphire[54–57] has a static dielectric constant which is larger than for the alumina films.

The dash–dot curve in Fig. 4 represents the dielectric function of Al_2O_3 produced by anodization in ammonium citrate as taken from papers by Harris.[9,10] These data are in fair agreement with ours except at $\tilde{\nu} < 300\ cm^{-1}$ where Harris's ϵ_1 values show a rapid and unphysical decrease which points at the extreme uncertainties in his evaluation for the lowest frequencies.

It is of some interest to compare our dielectric function for evaporated films of alumina with that for bulk sapphire (α-Al_2O_3).[11] The reflectance measurements by Barker[11] were represented in terms of a classical oscillator model with the dominant modes lying at 442- and 569-cm^{-1} frequencies for the ordinary ray and at 400- and 583-cm^{-1} frequencies for the extraordinary ray. Hence the locations of our absorption peaks do not strongly deviate from those found in sapphire.

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Meetings Calendar *continued from page 2725*

1983
August

28–2 Sept. 186th ACS Natl. Mtg., Wash., D.C. *A. T. Winstead, 1155 16th St. N.W., Wash., D.C. 20036*

November

7–11 APS Div. of Plasma Physics, Seattle *W. W. Havens, Jr., 335 E. 45 St., N. Y., N.Y. 10017*

1984

? **Optical Interference Coatings, 3rd OSA Topical Mtg.** *Mtgs. Dept., OSA, 1816 Jefferson Pl., Wash., D.C. 20036*

? ICO 1984 General Assembly, Japan *H. Gamo, 3812 Inlet Isle Dr., Corona del Mar, Calif. 92625*

April

8–13 187th ACS Natl. Mtg., St. Louis *A. T. Winstead, 1155 16th St. N.W., Wash., D.C. 20036*

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