Effect of Damping on Surface Plasmon Dispersion*

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The dispersion of surface plasmons at an air-metal interface has been studied experimentally using the method of attenuated total reflection. In the vicinity of the surface plasmon energy the dispersion curve was found to bend back toward the light line instead of increasing asymptotically to the surface plasmon energy at infinite momentum. We conclude that surface plasmon interactions must be characterized by a complete response-function surface rather than by a single dispersion curve.

Collective oscillations in electron density at the surface of a metal may be described in terms of surface plasmon waves.[1] These waves may be classified broadly as radiative or nonradiative in character; the latter property follows from the fact that the momentum along the surface, $\hbar k_s$, of a nonradiative surface plasmon of wave vector k_s is greater than that of an electromagnetic wave in vacuum of the same angular frequency ω. It is conventional[2] to represent dispersion of surface plasmons on a semi-infinite dielectric bounded by vacuum, for values of k_s small enough that hydrodynamic dispersion[3] is not important ($k_s \sim \omega/c$), by the equation

$$k_s = (\omega/c)[\epsilon/(\epsilon+1)]^{1/2}, \qquad (1)$$

where $\epsilon = \epsilon_1(\omega) + i\epsilon_2(\omega)$ is the complex dielectric function of the medium. If ϵ_2 is set equal to zero, the surface plasmon dispersion curve, i.e., a plot of ω versus k_s for the wave, goes asymptotically to the characteristic surface plasmon frequency ω_s for large wave vectors, i.e., for $\epsilon_1 \rightarrow -1$. If damping is included, i.e., $\epsilon_2 \neq 0$, the surface plasmon dispersion curve as defined by Eq. (1) does not increase monotonically to ω_s as k_s increases but instead, at some finite k_s value, turns back toward the light line. This is shown for Ag in Fig. 1, where the solid curve has been calculated from Eq. (1) using experimental values of ϵ_1 and ϵ_2 from the literature.[4,5] It was found that both sets of data from the literature and our own measurements of ϵ_1 and ϵ_2 for Ag gave essentially the same curve.

We have obtained experimental data relating to the shape of the surface plasmon dispersion curve. These data are shown by the points in Fig. 1. Previous experimental determinations of the dispersion of surface plasmons from electron-energy-loss measurements[6-8] have shown a monotonic increase toward the asymptote at ω_s as k_s increases. Also, attenuated-total-reflection techniques have been used to excite surface plasmons in metals[9-11] and in semiconductors,[12] and to examine the effect of surface roughness on the surface plasmon dispersion curve.[13] These observations have shown no indication of a bending back in the dispersion curve in the vicinity of ω_s.

Our experimental arrangement is essentially that originally proposed by Kretschmann and Raether,[11] and is shown in Fig. 2. A transparent semicylinder was cleaned and then a thin Ag film deposited by vacuum evaporation on the plane surface. Monochromatic, p-polarized light, incident through the curved surface of the semicylinder, was reflected from the semicylinder-Ag interface and the reflectance measured as a function of the

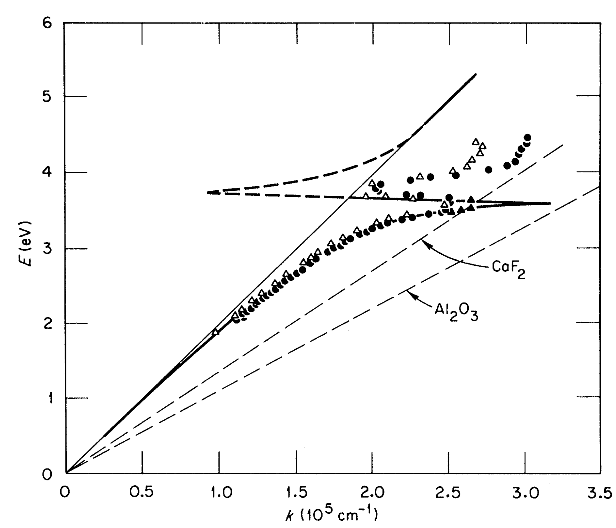

FIG. 1. Surface plasmon dispersion curve. Solid line, calculated from Eq. (1); open triangles, 340-Å-thick Ag film on CaF_2; circles, 290-Å, and filled triangles, 500-Å Ag films on sapphire. The dashed portion of the theoretical curve to the left of the light line is predicted from Eq. (1) and is presented for completeness but does not correspond to the existence of surface plasmons in this region.

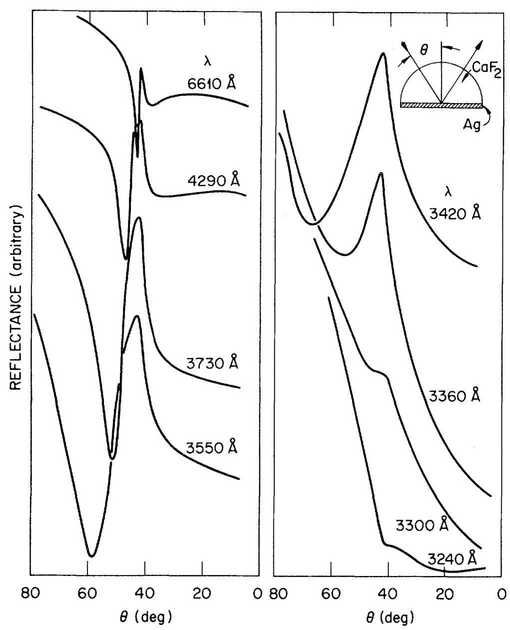

FIG. 2. Experimental curves of reflectance versus angle of incidence for 340 Å of Ag on a CaF_2 semicylinder and for different wavelengths.

angle of incidence θ. At an angle just greater than the critical angle for total internal reflection of the material of the semicylinder, a sharp minimum occurs in the reflectance. At this angle photons refracted along the semicylinder-Ag interface can excite surface plasmons associated with the Ag-vacuum surface. The angular position of the minimum in reflectance is governed by the condition

$$k_s = k_{\parallel} = (\omega/c)n \sin\theta,$$

where $k_{\parallel}$ is the component of the photon wave vector parallel to the semicylinder-Ag interface, and n is the index of refraction of the material of the semicylinder.

Figure 2 shows representative measurements of reflectance versus angle of incidence for photons of various wavelengths. The semicylinder was CaF_2 and the Ag film was 340 Å thick. The Ag film was vacuum evaporated, *in situ*, at 10^{-9} Torr and was not exposed to the atmosphere during measurements. The thickness was calculated from a least-squares fit to the reflectance versus angle of incidence based on Fresnel's equations. The thickness of the Ag film was chosen to be thin enough for the incident energy to be able to penetrate to the Ag-vacuum interface and excite surface plasmons, and thick enough that the dispersion curves are identical for the normal and tangential nonradiative surface plasmon modes in the Ag film. The variation of $k_{\parallel}$ with ω, calculated from the positions of the minima shown in Fig. 2 and using Eq. (2), are shown in Fig. 1. It is seen that agreement is obtained with the ω-versus-k_s variation calculated from Eq. (1) for regions to the right of the light line and for energies below the volume plasmon energy for Ag (3.75 eV), except for the regions with the largest k values. Also shown in Fig. 1 are two lines indicating the maximum $k_{\parallel}$ value which can be excited by this method, calculated from Eq. (2) with $\sin\theta = 1$ and the values of n for CaF_2 and sapphire in the vicinity of ω_s for the Ag-vacuum interface. It is seen that using CaF_2 we cannot excite as high k values as are calculated from Eq. (1). The observations were thus repeated using a 290-A-thick Ag film on a sapphire semicylinder. The thickness of this film was monitored with a quartz-crystal thickness monitor, and then the optical data, shown in Fig. 1, were obtained at atmospheric pressure. It is seen that the results are substantially the same as with the CaF_2 semicylinder and that the higher k values predicted by Eq. (1) are not obtained, although with the sapphire semicylinder this should be possible experimentally. It was thought that possibly the Ag film thickness might influence these results. Solutions of Fresnel's equations for the angle at which the reflectance is a minimum as a function of the thickness of the Ag film confirm the values obtained experimentally for both the CaF_2 and sapphire semicylinders. The maximum value of k which can be excited by this method is found to depend on the film thickness, but never becomes as great as predicted by Eq. (1). As an illustration, results for a 500-Å Ag film on sapphire are also shown in Fig. 1. Our calculations show that the data for this film represent approximately the largest k values which can be excited for a Ag film of any thickness on sapphire by this method.

The discrepancy between results from electron-energy-loss experiments and attenuated–total-reflectance experiments arises because the surface plasmon dispersion cannot be represented completely in terms of a single ω-versus-k relationship. Starting with the known optical constants of Ag, interesting differences are found in the calculated dispersion relations based on electron energy losses and on attenuated total reflection (optical absorption). This difference has not been noted before, theoretically or experimentally, to our knowledge. The explanation of this difference seems to lie in the fact that the dispersion curves are inferred from the respective experiments in different ways. In the usual electron-energy-loss experiment, a distribution of energy losses is measured at fixed momentum transfer $\hbar k$; the energy corresponding to the most probable energy loss to the surface plasmon field is determined and is plotted versus k to establish a single point on the surface plasmon dispersion curve. This procedure is repeated for various values of k until an experimental ω-versus-k curve can be established. The procedure followed in the attenuated-total-reflection experiment as described in this paper in essence corresponds to finding the direction of the incident photons for which the absorption is a maximum for a constant photon energy. A complete description of the surface plasmon, when damping is present, therefore requires a three-dimensional representation which gives some characteristic response of the surface plasmon in terms of k and ω, rather than a single ω-versus-k relation. A suitable generalized response-function surface can be derived from each set of experimental data if the proper correction factors are applied to the data to account for the different experimental conditions. A fuller description of these points will be submitted for publication in the near future.

The results obtained for $k_{\parallel}$ versus ω above the volume plasmon energy, i.e., the upper portions of the experimental curves in Fig. 1, are not fully understood in terms of a simple surface plasmon model at this time. These values were calculated using Eq. (2) with θ determined as before from the minimum in the reflectance-versus-angle data. However, ϵ_1 is greater than -1 in this energy region, and the minimum in the R-versus-θ curve presumably does not represent the excitation of surface waves.

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