Surface-plasmon dispersion relation: Shifts induced by the interaction with localized plasma resonances

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The interaction between the localized plasma resonances associated with small metal particles and surface plasmons on a nearby metal-dielectric interface has been observed. Shifts in the surface-plasmon dispersion relation and changes in the effective absorption of the metal particles (Ag-island resonances) resulting from this interaction were measured as a function of the separation d between the two structures. In our geometry, the two excitations are most strongly coupled for a separation $d \cong 25$ nm.

The surface-plasmon dispersion relation $\omega(k)$ displays the characteristic energy-momentum states for a TM (transverse magnetic) surface wave at a metal-dielectric interface. These states are modified when the surface plasmon interacts with surface roughness,[1] gratings,[2–4] dielectric overlayers,[5,6] and molecules,[7] resulting in a shift in $\omega(k)$. It has recently been observed that the excitation of surface plasmons and/or localized plasma resonances associated with small metal particles can lead to the amplification of local electromagnetic fields and the enhancement of various optical processes.[8–11] Motivated by these discoveries, several authors have investigated the coupling of plasma resonances in adjacent metal particles.[12] It has also been observed that the presence of a Ag-island film can improve the efficiency of light emission from a metal-insulator-metal tunnel junction.[13] This effect was attributed to the excitation of the dipole resonances of the islands by the evanescent waves associated with the nonradiative modes of the tunnel junction. This paper explores that interaction in greater detail and reports the observation and measurement of the shift in the surface-plasmon dispersion relation $\omega(k)$ induced by a metal-particle overlayer (island film) placed in close proximity to a metal-dielectric interface. Our results show that (1) there exists a thickness of the transparent spacer layer placed between the island film and the interface supporting the surface plasmon that maximizes the shift in $\omega(k)$, and (2) the effective absorption of the plasma resonance associated with the particles that make up the island film is a maximum for that same separation.

The samples for this investigation were prepared by thermal evaporation in an oil-free, cryogenically pumped ultrahigh vacuum system at pressures in the 10^{-8}-Torr range. In order to clearly distinguish changes in $\omega(k)$ induced by successive layers, the thin films were deposited in the stair-stepped configuration shown in Fig. 1. First a continuous silver film of thickness 50 nm was evaporated onto a glass substrate. After partial masking with a movable shutter, a lithium fluoride (LiF) layer of thickness d was deposited over a portion of the silver surface. Further masking preceded the slow (~ 0.5 Å/sec) deposition of a silver-island film of mass thickness 3 nm (the mass thickness is the value determined by a quartz-crystal film-thickness monitor). Each three-layer structure was prepared without breaking vacuum, but all subsequent measurements were made in the ambient laboratory atmosphere. The island films prepared in this way were gold in color and transmission measurements on witness samples showed the familiar anomalous absorption near $\lambda = 400$ nm that is characteristic of localized plasma resonances.[14] No discernable change in the optical properties of the island films was found over several deposition cycles with the same sample parameters.

Two types of measurements were made on the completed samples. In the first, the back surface of the glass substrate was optically contacted to a prism and the structure was examined in the usual ATR (attenuated total reflection) geometry shown as an inset in Fig. 2. The stepwise arrangement of the sample layers permitted a separate examination of each layer combination (Ag-air, Ag-LiF-air, and Ag–LiF–Ag-islands–air) by a translation of the optical probe beam that is incident on the sample

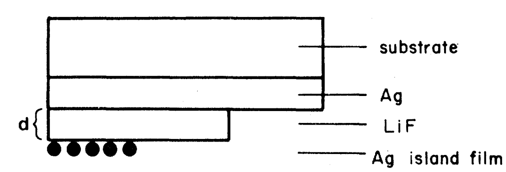

FIG. 1. Cross section of stair-stepped sample geometry used in the present experiment. The continuous silver film has a thickness of 50 nm. The thickness of the LiF spacer layer d was varied between 5 and 60 nm. The silver-island film had a mass thickness of 3 nm. All films were measured with a quartz-crystal thickness monitor.

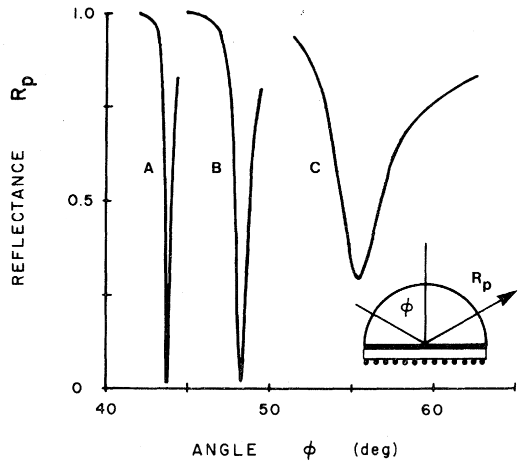

FIG. 2. Measured reflectivity R_p, as a function of the angle ϕ in the prism. In this case, the excitation wavelength was 514.5 nm and the spacer-layer thickness $d = 20$ nm. The minima represent surface-plasmon excitations on each portion of the sample. A: Ag-air; B: Ag-LiF-air; C: Ag—LiF—Ag-islands—air. Insert shows ATR geometry.

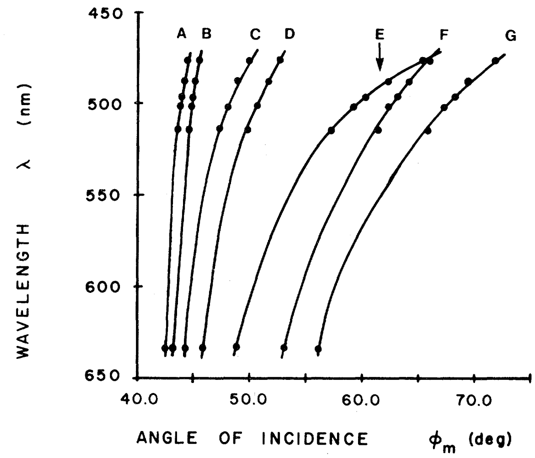

FIG. 3. Measured surface-plasmon dispersion relation (λ vs ϕ_m) shown for three values of spacer-layer thickness d. Curve A is that for the Ag-air interface. Curves B, D, and F correspond to Ag-LiF-air with $d = 5$, 25, and 60 nm, respectively. Curves C, E, and G show the modification introduced in each case by the addition of a 3-nm mass thickness Ag-island film.

through the glass prism. Measurements of the p-polarized reflectivity were made as a function of the angle ϕ for wavelengths available from argon-ion, helium-cadmium, and helium-neon lasers. The results of a typical measurement of the p-polarized reflectivity as a function of ϕ for $\lambda = 514.5$ nm and $d = 20$ nm are shown in Fig. 2. The sharp minimum at $\phi \cong 43°$ corresponds to the excitation of a surface plasmon at the Ag-air interface. By translating the beam and repeating the measurement, one finds that the addition of the LiF layer shifts the minimum to higher angle ϕ with only a small change in the width of the feature (as is well known). A further translation of the probe beam shows that the effect of the Ag-island film is not only an additional shift, but also a broader and shallower resonance, a fact that is easily explained by the absorption introduced by the island film.

The surface plasmon's propagation constant k is related to the angle ϕ_m at which the reflectivity is a minimum according to

$$k = n_p(2\pi/\lambda)\sin\phi_m \ , \quad (1)$$

where n_p is the refractive index of the prism. Plots of the measured dispersion relation (expressed, for convenience, as λ vs ϕ_m) for three values of the LiF spacer-layer thickness d are shown in Fig. 3. Curve A is that for the surface plasmon at the Ag-air interface. Curve B adjacent to it is that corresponding to the addition of 5 nm of LiF, and the next curve C, is that corresponding to the addition of the 3-nm Ag-island film. The remaining four curves are, in pairs, those for LiF spacer-layer thicknesses of $d = 25$ and 60 nm. The shift from the first curve induced by a particular LiF thickness is apparent in each case. The additional shift introduced by the island film is also evident, and increases in size for a given separation d as the wavelength approaches the center of the absorption band of the localized plasma resonance. It is significant to note that the island-induced shift in the surface-plasmon dispersion relation is greatest at each wavelength for the intermediate spacer-layer thickness $d = 25$ nm.

To explore this behavior in more detail, we measured the island-induced shift of $\omega(k)$, or $\lambda(\phi_m)$, for several values of the spacer-layer thickness d, and the results are shown for three wavelengths in Fig. 4. The quantity Δk is the difference in the measured surface-plasmon propagation constants for the Ag-LiF-island and Ag-LiF cases. Therefore, Δk represents the change in the propagation constant of the surface plasmon at Ag-LiF interface that results from the introduction of the island film. In the figure, Δk has been divided by $k_0 = 2\pi/\lambda$. It is clear, then, that for a given wavelength the influence of the Ag particles on the surface plasmon is a maximum at a distance $d \cong 25$ nm, and is most pronounced at photon energies closest to the localized plasmon resonance of the Ag-island film.

A second type of measurement on the three-layer structure of Fig. 1 examined more directly the optical properties of the localized plasma resonances. Measurements of the near-normal specular reflectivity of the island-LiF-Ag structure with light incident on the island-film side were made as a function of the wavelength λ. The results are shown for three values

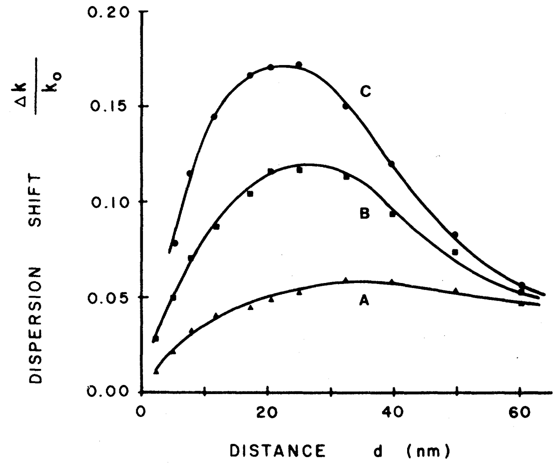

FIG. 4. Variation of the dispersion shift $\Delta k/k_0$, with spacer-layer thickness d, for three different wavelengths. The quantity Δk is the difference between the measured propagation constant k for the Ag–LiF–Ag-islands–air and the Ag-LiF-air cases. Here $k_0=\omega/c$. Curve A, $\lambda=632.8$ nm; curve B, $\lambda=514.5$ nm; curve C, $\lambda=476.5$ nm. Solid lines are drawn as guides to the eye.

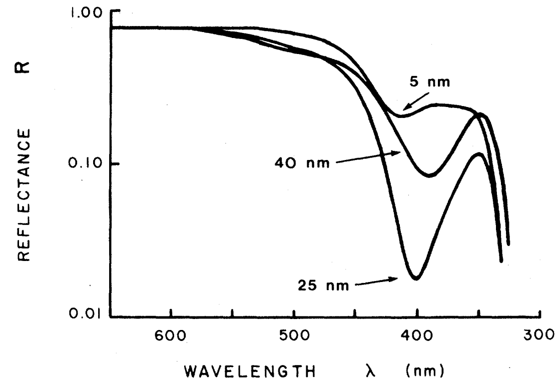

FIG. 5. Measured near-normal reflectance R as a function of wavelength. Curves are labeled for three spacer-layer thicknesses. The minima near $\lambda=400$ nm correspond to absorption by the silver islands. Note that rather strong absorption occurs for the intermediate thickness $d=25$ nm.

of the spacer-layer thickness d in Fig. 5. Superimposed on the shape of the familiar silver reflectivity curve are the minima near $\lambda=400$ nm that correspond to the absorption band of the silver islands. The deepest minimum (note the logarithm scale) occurs for the intermediate spacer-layer thickness, as might be expected from the results shown in Fig. 4. These experiments were repeated using magnesium fluoride (MgF_2), instead of LiF, spacer layers with essentially the same results.

Since the plasma oscillations associated with the individual constituents of Ag-island films can be treated as electric dipoles, the sample geometry used in the present experiments is reminiscent of earlier explorations of the properties of molecular dipoles placed near a conducting surface.[15,16] Drexhage,[15] for example, observed a strong dependence of the molecular fluorescent decay rate on the separation between molecule and metal surface. He explained this phenomenon as an interference effect arising from the superposition of radiated and reflected fields. More recent investigations have concentrated on the interaction between the molecules and surface plasmons.[17–19] In that case, the evanescent field of the surface plasmon can nonradiatively couple to the molecule, with the coupling efficiency following the strength of the evanescent field for large separation d, but diminishing rapidly at small d due to competitive near-field processes.[18] One such experimental effort showed a metal-molecule distance dependence, similar to that reported here, for the intensity of the molecular fluorescence near-field coupled to and reradiated by surface plasmons.[19] The earlier measurements by McCarthy and Lambe on light emission from the island-film–tunnel-junction system also showed the existence of an optimum spacer-layer thickness.[13]

In summary, we have reported measurements of the shift in the surface-plasmon dispersion relation induced by an interaction with localized plasma resonances in metal particles. We have characterized this interaction by measuring its strength as a function of the separation of the two silver structures supporting the two types of plasma resonances. We find that the coupling is strongest for a LiF spacer-layer thickness $d=250$ Å. Our results also indicate that the effective absorption of the silver islands is maximized when the coupling is strongest, a fact that suggests that the experimental geometry used in these experiments may offer a new direction for investigations of surface-enhanced optical processes involving localized plasma resonances.

ACKNOWLEDGMENT

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