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Coupled Surface-Plasmon Modes in Metal–Thin-Film–Vacuum Sandwiches

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The normal surface-plasmon modes for a thin-layered plasma bounded on one side by a semi-infinite plasma and on the other side by a vacuum are determined. The characteristic frequencies of the coupled modes resulting from surface oscillations of the plasma-plasma interface and the plasma-vacuum interface are found. The relevance of these results to recent experiments by MacRae, Müller, Lander, Morrison, and Phillips is indicated.

THE presence of cesium surface-plasma oscillations in a system in which cesium is adsorbed on a metal surface has recently been postulated.[1,2] Callcott and MacRae have observed an energy loss in photoelectron emission from nickel coated with a few layers of cesium.[1] They suggest that this energy loss may be indicative of the excitation of a solid-cesium surface plasmon. More recently, MacRae, Müller, Lander, Morrison, and Phillips have reported characteristic energy losses in back-scattered electrons in low-energy electron diffraction studies from cesium-covered tungsten surfaces which they assert to be evidence for the excitation of surface plasmons in the cesium layer. Because of the different crystal structure of the cesium thin film compared to its bulk structure, the electron density is different in the layer and consequently the surface-plasmon frequency $\omega_s=(4\pi ne^2/m)^{1/2}/\sqrt{2}$ is different for a layered structure than for a semi-infinite plasma. Here, n is the free-electron density.

It is the purpose of this note to determine the normal surface-plasma modes of a thin layer of a solid-cesium plasma, bounded on one side by a semi-infinite plasma corresponding to the nickel or tungsten substrate and on the other side by a vacuum. We will extend some of the ideas put forth by Ritchie, Ferrell, and Stern for treating thin plasma films.[3–5]

Following Stern and Ferrell, consider a semi-infinite plasma in the half-space $z\leq 0$ characterized by a dielectric function $\epsilon_M(0,\omega)=1-\omega_m^2/\omega^2$ with ω_m the plasma frequency of the metal. In the region $0\leq z\leq \tau$, another thin-layered plasma is located with a dielectric function $\epsilon_c(0,\omega)=1-\omega_c^2/\omega^2$. The vacuum is in the region $z>\tau$. The electric potentials in the three regions, from surface-polarization charge, are given by

$$\varphi_M(x,z,t)=2\varphi_0\cos(kx-\omega t)e^{-k|z|}\,,\qquad z\leq 0$$
$$\varphi_c(x,z,t)=\cos(kx-\omega t)(Ae^{kz}+Be^{-kz})\,,\qquad 0\leq z\leq \tau$$
$$\varphi_v(x,z,t)=\cos(kx-\omega t)De^{-k|\tau-z|}\,,\qquad z\geq \tau\,.$$

At each boundary, continuity of the transverse electric field,

$$\frac{\partial\varphi_i}{\partial x}=\frac{\partial\varphi_j}{\partial x}\bigg|_{z=0,\tau}$$

and continuity of the normal electric displacement

$$\epsilon_i\frac{\partial\varphi_i}{\partial z}=\epsilon_j\frac{\partial\varphi_j}{\partial z}\bigg|_{z=0,\tau}$$

give four equations, three of which are used to determine the constants A, B, and C. The fourth equation yields the eigenvalues through

$$\frac{\epsilon_m}{\epsilon_c}=\frac{-1+\gamma e^{-2k\tau}}{1+\gamma e^{-2k\tau}} \tag{1}$$

with

$$\gamma=\frac{\epsilon_c-1}{\epsilon_c+1}\,. \tag{2}$$

Introducing the frequency-dependent dielectric functions, Eqs. (1) and (2) are solved to yield the dispersion relation

$$\omega^2=\tfrac{1}{8}\{4\omega_c^2+2\omega_m^2\pm[(4\omega_c^2+2\omega_m^2)^2 -16(\omega_c^2\omega_m^2(1+e^{-2k\tau})+\omega_c^4(1-e^{-2k\tau}))]^{1/2}\}\,. \tag{3}$$

We shall look at certain limiting cases of the eigenvalues given by Eq. (3).

(*a*) *Thick cesium film in which* $e^{-2k\tau}\to 0$. In this limit, Eq. (3) gives two branches

$$\omega_+=(\omega_M^2+\omega_c^2)^{1/2}/\sqrt{2}\,,\quad \omega_-=\omega_c/\sqrt{2}\,.$$

These solutions are just the eigenfrequencies of an uncoupled cesium-metal interface and a cesium-vacuum interface as they should be when the two interfaces are far apart and thus do not interfere.

(*b*) *Thin cesium film in which* $e^{-k\tau}\to 1$;

$$\omega_+=\omega_M/\sqrt{2}\,,\quad \omega_-=\omega_c\,.$$

The cesium does not affect the metal surface-plasmon frequency as evidenced by the ω_+ solution. On the other hand, if there is to be a characteristic frequency in the cesium, it must be at the bulk-plasma frequency since a zero thickness film has no surface layer. This, however, may be a metaphysical problem.

[1] T. A. Callcott and A. U. MacRae, Phys. Rev. **178**, 966 (1969).
[2] A. U. MacRae, K. Müller, J. J. Lander, J. Morrison, and J. C. Phillips, Phys. Rev. Letters **22**, 1048 (1969).
[3] R. H. Ritchie, Phys. Rev. **106**, 874 (1957).
[4] R. A. Ferrell, Phys. Rev. **111**, 1214 (1958).
[5] E. A. Stern and R. A. Ferrell, Phys. Rev. **120**, 130 (1960).

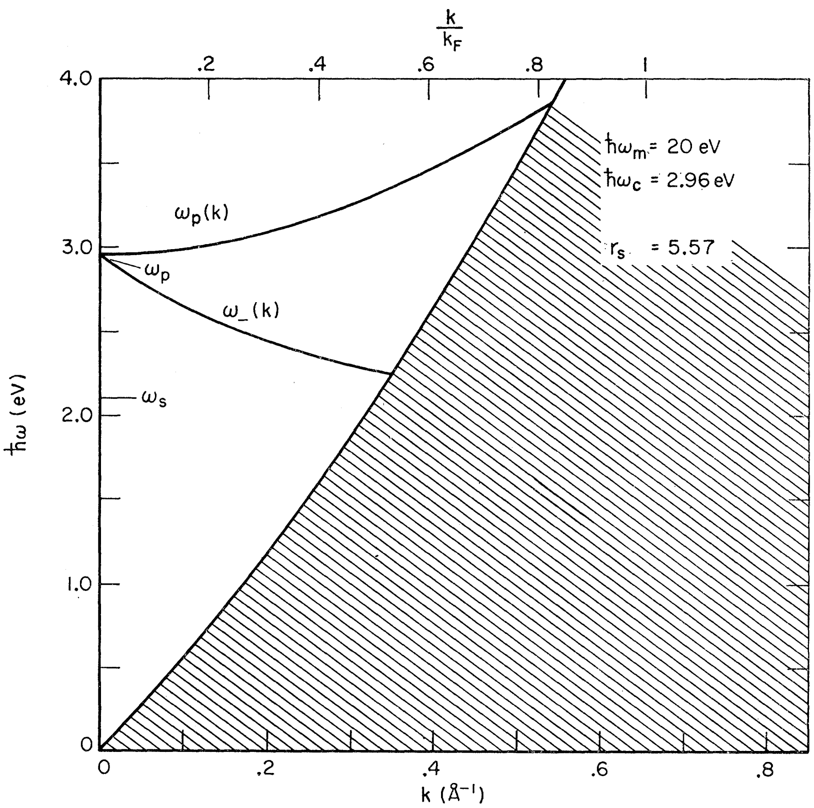

FIG. 1. Dispersion relations for electron excitations in a cesium layer bounded by a metal and a vacuum. $\omega_p(k)$ is the cesium volume-plasmon dispersion, $\omega_-(k)$ the coupled surface-plasmon dispersion, and the cross-hatched area is the region of pair excitations. The wave-vector scale at the top is normalized to the cesium Fermi wave vector, whereas the bottom scale is in inverse angstroms.

(*c*) *Cesium film bounded by a vacuum on both sides amounts to setting* $\omega_m=0$ *and thus* $\epsilon_m=1$ *as in vacuum.*

$$\omega_{(\pm)}=(\omega_c/\sqrt{2})(1\pm e^{-k\tau})^{1/2}. \quad (4)$$

This is the standard thin-film result obtained previously by Ritchie and Stern and Ferrell.[3,5] It is, however, not the relevant solution to the metal–thin-cesium-layer–vacuum sandwich.

(*d*) *Thin film with dispersion.* Equation (3) has been numerically evaluated with $\hbar\omega_m=20$ eV, a typical metal value, $\hbar\omega_c=2.96$ eV, the value appropriate for solid cesium, and $\tau=2.5$ Å. The dispersion relation for the ω_- branch is drawn in Fig. 1. Also drawn is a schematic bulk-plasmon dispersion curve. The cross-hatched area corresponds to the region of electron-hole pair excitations in which the left-hand limit is given by $E_{e-h}=\hbar^2(k^2+2kk_F)/2m$.[6] It is seen that the ω_- branch of the coupled surface-plasmon mode merges into the continuum of cesium pair excitations as the characteristic frequency is reduced to that of a cesium-vacuum interface. Even with the possibility of dispersion in the coupled mode, the cesium surface-plasmon frequency may never be realized because of the increased damping as the coupled-mode wavelength decreases. Finally, we note that Fig. 1 should be rescaled according to the true free-electron density in the cesium layer in order to make a direct comparison with presently available experimental results.

We are now left with the problem of determining what is responsible for the energy loss at 1.5–2.4 eV as the multilayers of cesium are deposited on the tungsten. To do this, we contrast the coupled surface-plasmon mode analysis presented here with the "zeroth-order approximation" given by MacRae *et al.*[2] They assume "that the inelastic scattering is associated with the emission of surface plasmons defined by $\text{Re}\,\epsilon(\omega)=-1$." As seen in the analysis given here, the characteristic frequencies of surface plasmons for the three-component structure are defined by a more complicated condition, expressed in Eqs. (1)–(3). MacRae *et al.* then claim that for a thin cesium film on a tungsten substrate, the surface-plasmon mode splits into two branches defined by the vacuum–thin-film–vacuum equation given in case *c*. They assume that the ω branch is responsible for the measured loss and that the dependence on film thickness is qualitatively described by Eq. (4). It is felt that the generalized result given by Eq. (3) and treated in case *d* here for a metal–thin-plasma–vacuum configuration is a more realistic model of a tungsten–thin-cesium-layer–vacuum configuration than the vacuum–thin-plasma–vacuum configuration assumed by MacRae *et al.*[2]

Regarding the energy loss, if a collective oscillation is excited in the thin cesium layer, then the plasmon frequency is given by Eq. (3) for a cesium electron gas

[6] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (McGraw-Hill Book Co., New York, 1967), p. 200.

with a density considerably less than that in solid cesium when we deal with only a few (less than about five) cesium layers. This can occur for two distinctly different reasons. As seen in Fig. 1 of Ref. 2, the areal density of the cesium lattice constantly increases from an initial low density as the evaporation time and thus coverage increase. The initial density and consequently the free-electron density is thus less than in metallic cesium. Second, as is well known in the theory of alkali adsorption, for cesium to reduce the work function, considerable charge transfer from the cesium to the metal must occur, thus making for a much smaller effective electron density in the region of the adsorbed cesium.[7,8] Put another way, if a thin cesium layer with a work function ϕ_c is placed upon a tungsten substrate with a work function $\phi_w > \phi_c$, sufficient electron charge would have to flow from the cesium to the tungsten in order that a dipole layer with a potential drop of $\phi_w - \phi_c$ could form and bring the Fermi levels of the two materials into coincidence. If the cesium is sufficiently thick, this flow of electrons will not appreciably affect the electron density in the cesium layer. On the other hand, if one is dealing with a layer one to three atoms thick, losing one electron per surface atom will very much reduce the resulting electron density in the cesium layer and thus, as seems to be observed experimentally, the energy of coupled surface-plasmon modes will be much smaller. As the coverage is increased to the point where the thick-film limit is applicable, the cesium surface plasmon, discussed in case *a*, will appear.

Next we note that the energy loss first appears experimentally at 1.5 eV in the thin layer. Equation (4) describing the vacuum–thin-film–vacuum surface-plasmon modes has the ω_- branch going continuously to zero. Thus, Eq. (4) is not consistent with the experimental observation that as τ goes to zero the characteristic energy loss to a surface-plasmon mode goes to 1.5 eV. On the other hand, Eq. (3), derived here, shows that as the cesium layer becomes thinner, the ω_- branch approaches a nonzero limit which could correspond to a cesium plasmon for a lower-density electron gas, in accord with the experimental observations in which the energy loss goes to 1.5 eV rather than zero. Put another way, as the thickness approaches zero, $\omega_- \rightarrow [4\pi n(\tau)e^2/m]^{1/2}$, where we have explicitly written the electron density as a function of thickness for the reasons mentioned in the previous paragraph. Thus, even though the ω_- solution of Eq. (3) approaches ω_c as τ goes to zero, if $n(\tau) \rightarrow$ small, the ω_- solution can decrease without going to zero, as is evidenced experimentally. This decrease in frequency occurs for a distinctly different reason than the interference effects causing the ω_- solution of Eq. (4) to decrease. It is the decreasing cesium electron density as the cesium becomes thinner and not the interference effects implicit in the ω_- solution of Eq. (4) that we feel are responsible for the drop in the characteristic cesium "surface-plasmon" loss.

Finally, we note the possible role played by retardation effects in the interaction between the electric fields at the two interfaces. Economou has presented a detailed study of the role of retardation in various sandwich configurations of metals and dielectrics.[9] In general, he finds that for wave numbers less than $k_p = \omega_p/c$, with c the speed of light, retardation will qualitatively alter the form of the surface-plasmon dispersion curve and, in fact, may cause some of the characteristic solutions of Eq. (3) to go to zero at extremely low k. For $\hbar\omega_p \approx 3$ eV, as in the cesium layer, $k_p \approx 10^{-3}$ Å^{-1}. However, the available phase space and density of surface-plasmon states is so small in this region that the probability of exciting a $k \lesssim k_p$ plasmon is vanishingly small compared to the probability of exciting one in the $k_p \lesssim k \lesssim k_{\max}$ region ($k_{\max} \approx 0.2$ Å^{-1}, the point where the plasmon curve merges into the pair continuum). The instantaneous analysis implicit in Eq. (3) should suffice, therefore, for interpretation of surface-plasmon excitation data, and for this reason retardation effects, thoroughly discussed by Economou,[9] are neglected here.

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[7] J. W. Gadzuk, Surface Sci. **6**, 133 (1967).

[8] J. W. Gadzuk, in *Proceedings of the Fourth International Materials Symposium on the Structure and Chemistry of Solid Surfaces, Berkeley, California, 1968* (John Wiley & Sons, Inc., New York, 1969).

[9] E. N. Economou, Phys. Rev. **182**, 539 (1969).