Dispersion of surface plasmons and phonons in inhomogeneous media

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The dispersion relation of surface plasmons or phonons is obtained, by solving Maxwell's equations, for the case that the dielectric function $\epsilon(\omega)$ has a small exponential variation below the surface, perpendicular to the propagation direction. Only the usual two branches are found. The lower one exhibits the properties, at large propagation vector, that the limiting ω is determined by the surface value of ϵ and the shape depends on the spatial extent of the variation in ϵ.

In an earlier paper[1] we discussed the guided surface modes that can propagate in a planar semi-infinite medium whose dielectric function varies with distance below the surface. In that paper and the present one we take x to be the propagation direction, z is the direction of the gradient in ϵ, and $z=0$ is the plane separating the inhomogeneous medium ($z<0$) from a homogeneous medium above. The amplitudes of the guided modes, while exponentially decaying for $z>0$, were found to be oscillatory for some range, depending on mode number, below $z=0$, before again decaying exponentially as z approached $-\infty$. In the present paper we consider surface plasmons and phonons, whose amplitudes decrease monotonically, although not necessarily exponentially, with increasing $|z|$ in the medium with varying ϵ. We find that the properties of the plasmon dispersion at large k_x are determined by the value and gradient of ϵ at the surface. In the limit of very small spatial extent of the variation in ϵ we obtain a dispersion relation similar to, although not identical with, that obtained by Guidotti *et al.* in treating the same problem for metals.[2] We show that this dispersion relation does not, however, lead to an extra branch in the surface-plasmon dispersion as claimed by them.

One question of interest here is the effect on surface plasmons of a semiconductor accumulation or depletion layer. In past treatments of this problem the graded-index region has been replaced by a step-function discontinuity between the bulk, with dielectric constant $-|\epsilon_b|$, and a thin layer of constant $\epsilon\neq-|\epsilon_b|$ representing the surface.[3] Another case of interest is that of a graded index arising from a composition gradient in a polar material due, for example, to in or out diffusion of impurities or one of the constituents during crystal growth. To cover both cases, we may write the dielectric constant in the usual form,[4] neglecting damping,

$$\epsilon(\omega;z)=\frac{S\omega_t^2}{\omega_t^2-\omega^2}+\epsilon_\infty\left(1-\frac{\omega_p^2}{\omega^2}\right), \tag{1}$$

where S, ω_t, ϵ_∞, and ω_p are all functions of z. (We use local theory, as is generally done for the systems we are mainly concerned with here.) As a model system for the polar crystal we may consider Se-diffused CdS, i.e., $CdSe_yS_{1-y}$, where y is a function of z. From the results of Verleur and Barker,[5] for small y the quantities ω_t, the principal TO-phonon frequency of the host lattice, S, its oscillator strength, and ϵ_∞, the high-frequency dielectric constant, all vary linearly with y. Except for ω close to ω_t, ϵ will then also vary linearly with y. From studies of Se diffusion in CdS,[6] $y=y_0e^{z/d}$, where y_0 represents the surface concentration and d a diffusion depth. For small y, therefore, except for ω close to ω_t, the z dependence of ϵ may be written

$$\epsilon(\omega;z)=\epsilon_b+\Delta\epsilon e^{z/d}, \tag{2}$$

where $\Delta\epsilon$, the difference between surface and bulk values, depends on y_0, $d\omega_t/dy$, dS/dy, $d\epsilon_\infty/dy$, etc. For the plasmon case, the z dependence arises from the dependence of ω_p^2 ($=4\pi Ne^2/m^*\epsilon_\infty$) on the carrier concentration N and, in some cases, the effective mass m^*. The variation of N or ϵ with z for an accumulation or depletion layer can be approximated by (2) with a suitably chosen d. From (1) we calculate, for the plasmon case,

$$\Delta\epsilon/\epsilon_b=-(\omega_{pb}^2-\omega_{ps}^2)/(\omega_{pb}^2-\omega^2), \tag{3}$$

where the subscripts s and b indicate surface and bulk values, respectively. Note that, although both $\Delta\epsilon$ and ϵ_b approach ∞ as $\omega\to0$, their ratio remains finite.

As in the case of homogeneous media, the surface plasmons and phonons must be transverse-magnetic modes to satisfy the boundary conditions at $z=0$. For simplicity, we take the inhomogeneous medium to be isotropic. Assuming a solution of the wave equation in the form

$$H=H_y=\epsilon^{1/2}(z)F(z)e^{i(k_xx-\omega t)} \tag{4}$$

and inserting this into the wave equation, we obtain

$$\frac{d^2F}{dz^2}+\left[\frac{1}{2\epsilon}\frac{d^2\epsilon}{dz^2}-\frac{3}{4\epsilon^2}\left(\frac{d\epsilon}{dz}\right)^2+\epsilon\frac{\omega^2}{c^2}-k_x^2\right]F=0. \tag{5}$$

Although they could be neglected at optical frequencies,[1] the terms involving derivatives of ϵ cannot be neglected in the frequency range where $\epsilon < 0$. With ϵ in the form (2), we can solve Eq. (5) in terms of known functions when

$$|\Delta\epsilon/\epsilon_b| \ll 1, \tag{6}$$

and we limit further discussion to cases where (6) is satisfied. For surface phonons in our model system, provided $y \lesssim 0.1$, Eq. (6) can be satisfied over most of the range in which $\epsilon < 0$, with only the regions of ω close to ω_t and very close to ω_l, the LO-phonon frequency, excluded. For plasmons, as seen from Eq. (3), Eq. (6) can be satisfied, provided (i) ω_{ps}^2 is close to ω_{pb}^2 and (ii) ω does not come too close to ω_{pb} or ω_{ps}. To achieve $|\Delta\epsilon/\epsilon_b| \leq 0.15$, for example, in the range $0 \leq \omega \leq 0.95\ \omega_{pb}$ requires $(N_s - N_b)/N_b = 0.015$ independent of the material. Larger values of $(N_s - N_b)/N_b$ may be tolerated if the surface plasmons do not attain such high frequencies. No restriction need be made on the value of d.

When $|\Delta\epsilon/\epsilon_b|$ is small, it is useful to expand ϵ and ϵ^2 in the denominators of Eq. (5) in terms of this quantity and, after changing variable to $u = -z/2d$, we may rewrite (5),

$$\frac{d^2F}{du^2} + \left[-\nu^2 + \beta^2 e^{-2u} - 5\left(\frac{\Delta\epsilon}{\epsilon_b}\right)^2 e^{-4u} + \cdots\right]F = 0, \tag{7}$$

where

$$\nu = 2dp_0 = 2d\,(k_x^2 - \epsilon_b\omega^2/c^2)^{1/2}, \tag{8}$$

$$\beta^2 = [(4d^2\omega^2/c^2) + (2/\epsilon_b)]\Delta\epsilon . \tag{9}$$

The quantity p_0 is the reciprocal of the decay length of the surface plasmon or phonon for the case $\Delta\epsilon = 0$, i.e., the homogeneous medium. Since the remaining terms in the brackets of Eq. (7) are all ascending powers of $(\Delta\epsilon/\epsilon_b)e^{-2u}$, when

$$|\beta^2| \gg 5(\Delta\epsilon/\epsilon_b)^2, \tag{10}$$

the term in $(\Delta\epsilon/\epsilon_b)^2$ and all the succeeding terms may be neglected. In what follows we shall assume that (10) is satisfied as well as (6). The solution of (7) may then be written in terms of Bessel functions. Imposing the condition that the field must remain finite as $z \to -\infty$, we obtain, using (4),

$$H_y = A\epsilon^{1/2}(z)J_\nu(\beta e^{z/2d})e^{i(k_x x - \omega t)}, \tag{11}$$

where A is an arbitrary constant.

We take the medium above $z = 0$ to be vacuum and assume H_y decays exponentially there. Applying the requirements of continuity of H_y and E_x to the solutions valid above and below $z = 0$, we arrive at the dispersion relation for the surface plasmons or phonons

$$\frac{\beta}{J_\nu(\beta)}\ \frac{dJ_\nu(\beta)}{d\beta} = -2\epsilon_s dp_2 - \frac{\Delta\epsilon}{\epsilon_s}, \tag{12}$$

where $p_2 = (k_x^2 - \omega^2/c^2)^{1/2}$, the reciprocal of the decay length in vacuum. This dispersion relation may be simplified at the extremes of large k_x and, for the plasmons, small k_x. In the latter limit, since $\epsilon_s \to \infty$ while all terms not involving p_2 are finite, p_2 must tend to zero or $k_x \simeq \omega/c$ just as for the homogeneous case. In the limit of large k_x, the order of the Bessel function, given by (8), goes to ∞. Since the surface phonon or plasmon frequency must remain finite as $k_x \to \infty$, we expect β to approach some constant value. We may then use the asymptotic form for the left-hand side of (12), which yields ν plus a remainder of order $(1/\nu)$.[7] Neglecting the remainder, we obtain the dispersion relation

$$2d(p_0 + \epsilon_s p_2) = -\Delta\epsilon/\epsilon_s, \quad k_x \text{ large}. \tag{13}$$

Using the definitions of p_0 and p_2, squaring to eliminate radicals and dropping terms higher than first order in $\Delta\epsilon/\epsilon$, we obtain from (13) a quadratic equation for k_x^2. The solution, normalized by dividing through by $K^2 = \Omega^2/c^2$, where Ω is the frequency for which $\epsilon_b = 0$, is

$$\frac{k_x^2}{K^2} = \frac{\omega^2}{\Omega^2}\,\frac{\epsilon_s^2 - \epsilon_b}{\epsilon_s^2 - 1} \pm \frac{\omega}{\Omega}\,\frac{\Delta\epsilon}{Kd}\,\frac{(1-\epsilon_b)^{1/2}}{(\epsilon_s^2 - 1)^{3/2}}, \quad k_x \text{ large}, \tag{14}$$

where the plus sign is required for the case $\Delta\epsilon < 0$ (accumulation layer) and the minus sign for $\Delta\epsilon > 0$ (depletion layer). If we allow $\Delta\epsilon \to 0$ in (14), the second term vanishes, $\epsilon_s \to \epsilon_b$ and we recapture the dispersion relation for the homogeneous semi-infinite medium in vacuum. In the limit $k_x \to \infty$, we will come to a limiting value $\omega_{1\mathrm{im}}$ given, according to (14), by the condition $\epsilon_s(\omega_{1\mathrm{im}}) = -1$. It follows that the limiting value or plateau of ω vs k_x for an accumulation layer will lie above that for the homogeneous case (i.e., flat bands to the surface), while for a depletion layer it will lie below.

We now show that, within the range of validity of the present approximations, where the dispersion curves depart from that for the homogeneous case, that of an accumulation layer will always lie above it, that of a depletion layer will always lie below. With k_x large, both p_0 and p_2 are large. Since $\Delta\epsilon/\epsilon_s$ must be small, we expect the k_x^2 that satisfies (13) to be given, at least to a good approximation, by a term that satisfies $p_0 + \epsilon_s p_2 = 0$ plus a smaller correction term involving $\Delta\epsilon$. Equation (14) is, in fact, of this form with the first term giving precisely the value of k_x^2 required to make $p_0 + \epsilon_s p_2$ vanish. At a frequency ω for which all three curves could exist (i.e., $\omega \lesssim \omega_{1\mathrm{im}}$ for a depletion layer), $|\epsilon_s|$ would be largest for the accumulation layer and smallest for the depletion layer. Since $|\epsilon_s| \simeq 1$ in the frequency range where (13) and (14) are valid, the size of the first term in k_x^2 will be smallest for the accumulation layer, largest for the depletion layer. The second term on the right-hand side of

(14) will tend to bring both the values of k_x^2 for accumulation and depletion layers back toward the value for the homogeneous case, but, as already pointed out, this term must be smaller than the others in the present approximation. We conclude, therefore, that ω vs k_x for the accumulation layer will lie above that of the homogeneous case which in turn is above that of the depletion layer. Behavior characteristic of a depletion layer has been seen experimentally by Marschall *et al.*[8] Unfortunately, $\Delta\epsilon/\epsilon_b$ for their sample is somewhat too large for (14) to apply accurately at large k_x.

Although the dispersion relation (12) is valid for arbitrary d, provided (10) is satisfied, the requirement that the second term of (14) be smaller than the first places a lower limit on the values of Kd for which that equation is valid. For a depletion layer, when $\epsilon_s \approx 1.1$, for example, validity of (14) requires $Kd \geq 0.3$. If we take Ω in the range 5×10^{13} to 5×10^{14} sec^{-1}, which includes LO-phonon frequencies of many materials and the plasma frequencies of some typical semiconductors, K varies from 1.7×10^3 to 1.7×10^4 cm^{-1}. To achieve $Kd > 0.3$ requires $d > 1.8$ μm at 5×10^{13} sec^{-1}, > 0.18 μm at 5×10^{14} sec^{-1}. In or out diffusion could certainly create d's of the magnitude required. Without diffusion or other special treatment some accumulation or depletion layer widths are in this range but many are not. To treat layers with smaller d's it would be necessary to carry (14) to higher order in $\Delta\epsilon/\epsilon$.

In the plasmon case for small d values it is possible to simplify the dispersion relation (12) for all k_x. With small enough d, $4d^2(\omega^2/c^2)\,\Delta\epsilon \ll 2\Delta\epsilon/\epsilon_b$ throughout the permissible range of ω. $|\beta|$ is then of the order of $|(\Delta\epsilon/\epsilon_b)^{1/2}|$. [Condition (10) is still satisfied since $|\Delta\epsilon/\epsilon_b|$ is small.] We may then expand the Bessel functions in (12), dropping terms quadratic and higher order in $(\Delta\epsilon/\epsilon_b)$, as has been done throughout. The dispersion relation then becomes, for small d,

$$d(p_0+\epsilon_s p_2) = -\frac{\Delta\epsilon}{\epsilon_b}\,\frac{dp_0-\epsilon_b\omega^2 d^2/c^2}{1+2dp_0} \quad . \tag{15}$$

In the limit of large k_x, $\epsilon_b(\omega^2 d^2/c^2) \ll p_0 d$, and if $p_0 d \gg 0.5$, Eq. (15) goes over to (13), to terms linear in $\Delta\epsilon/\epsilon_b$. This enables us to determine how large k_x must be for (13) and (14) to be valid. Using the definition of p_0, we find that the requirement is

$$\frac{k_x^2}{K^2} \gg \frac{0.25}{K^2 d^2} - |\epsilon_b|\,\frac{\omega^2}{\Omega^2} \quad . \tag{16}$$

For $Kd = 0.3$ this leads to (13) and (14) being valid if $k_x \gg 1.4$ K, since the second term on the right-hand side is of the order of unity.

The dispersion of surface plasmons in metals with ϵ varying according to (2) and $|\Delta\epsilon/\epsilon_b| \ll 1$ has been studied recently by Guidotti, Rice, and Lemberg[2] for the case of very small d. In our terminology this becomes the case of $\beta \simeq |(\Delta\epsilon/\epsilon_b)^{1/2}|$. Solving the wave equation, after a couple of substitutions, by a series expansion which they cut off so as to exclude terms higher than linear in $|\Delta\epsilon/\epsilon_b|$, they obtain a solution identical to that which can be obtained from our solution (11) by expanding the Bessel function keeping terms no higher than linear in $\Delta\epsilon/\epsilon_b$.[9] They also obtain a dispersion relation similar to (15). The relation differs from (15) only in having an additional factor $[1+d(p_0+\epsilon_s p_2)]^{-1}$ on the left-hand side. [It should be noted that they claim their dispersion relation to be valid only for small $k_x d$, but examination of their solution shows that this is an unnecessary restriction. The restrictions actually required for the validity of their dispersion relation are just those required for the validity of (15).] Since the coefficient of $(\Delta\epsilon/\epsilon_b)$ on the right of (15) is $\lesssim 1$, it is easily seen, either from (15) or from their dispersion relation, that $d(p_0+\epsilon_s p_2)$ is of order $|\Delta\epsilon/\epsilon_b|$. The additional factor in their expression then makes little difference, essentially adding a term of order $|(\Delta\epsilon/\epsilon_b)|^2$. However, plotting their dispersion relation for small k_x, $\omega_{pb} = 7$ eV $= 10.6\times 10^{15}$ sec^{-1}, $N_s = 1.1\,N_b$, and neglecting the imaginary part of ϵ, they find an additional branch lying between the usual surface plasmon branch and the photon branch. This additional branch, called branch II, is quite flat and has ω's lying between ω_{pb} and $\omega_{ps} = (1.1)^{1/2}\,\omega_{pb}$. When the data of their Fig. 4 are inserted into (3), it is found that $|\Delta\epsilon/\epsilon_b| \simeq 1.4$ for typical points on branch II. The dispersion relations are, of course, not valid for such $|\Delta\epsilon/\epsilon_b|$ and one cannot conclude that such a branch exists. Indeed there appears no *a priori* reason why such a branch should exist for ϵ in the form (2), unless perhaps dropping the condition $|\Delta\epsilon/\epsilon_b| \ll 1$ leads to the occurrence of some type of discontinuity. It is well known that the presence of a second interface sufficiently close to the first that the charge fluctuations of the two surfaces interact causes a new branch to arise. In the present situation, with $\Delta\epsilon$ assumed to decay exponentially, the second interface is at infinite distance from the one at $z = 0$, and the fields there are zero. This in fact constitutes one of the computational advantages of using the form (2) for ϵ rather than assuming a discontinuous ϵ or thin layer on top of the conductor.

In summary, we have obtained a generally valid dispersion relation for surface plasmons or phonons in samples with $\epsilon = \epsilon_b + \Delta\epsilon\, e^{z/d}$, where $|\Delta\epsilon| \ll |\epsilon_b|$ and $|(4d^2\omega^2/c^2 + 2/\epsilon_b)\,\Delta\epsilon| \gg (\Delta\epsilon/\epsilon_b)^2$. Although little difference from the dispersion for the case $\Delta\epsilon = 0$ is expected at small k_x, there will be visible effects at large k_x. For the plasmon case, with d

within the limits discussed, knowledge of the limiting value of ω at large k_x will make it possible to determine the carrier concentration at the surface. With this and knowledge of the bulk carrier concentration, the value of d can be determined from the shape of the dispersion curve at large k_x.

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[9]For knowledge of their solution I am indebted to Dr. Rice, who kindly supplied a preprint of a paper by Rice, Guidotti, Lemberg, Murphy, and Bloch [Adv. Chem. Phys. (to be published)], containing a more detailed discussion of the work.