Impedance of a thin film in the presence of spatial dispersion and the problem of additional boundary conditions

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We have calculated the surface impedance of a thin, spatially dispersive, dielectric film deposited on a metal substrate for two commonly used forms of the additional boundary conditions (ABC's) at the film-vacuum and film-substrate interfaces. The reflectivity has been calculated from the surface impedance for frequencies in the vicinity of the resonance frequency of the film, and numerical results are presented for the case of a ZnSe film on an Al substrate. The results for very thin films show not only quantitative but also qualitative differences between the predictions of the two ABC's that should enable a choice to be made between them on the basis of experimental reflectivity data. An approximate analytic expression for the reflectivity is obtained in the limit of very small film thicknesses, and its range of validity determined.

At the present time there exists a large amount of experimental and theoretical work devoted to the problem of the choice of additional boundary conditions. As is well known, this problem arises on taking into account the additional light waves that are present in a crystal when spatial dispersion is taken into account (see Ref. 1 and the literature cited therein). The relatively weak sensitivity of existing experimental data to the form of the additional boundary conditions, and their great variety, leaves a great deal of room for speculation about their nature.

In this paper we would like to direct attention to new analytical possibilities that are opened up in the investigation of thin, macroscopic films with a thickness $d \ll c/\omega n_i(\omega)$, where $n_i(\omega)$ is the refractive index of normal waves at frequency ω.

Under this condition, as will be shown below, the optical properties of a thin film in the vicinity of its resonances depend fundamentally on the form of the additional boundary conditions, which can be seen directly from the frequency dependence of the film's impedance.

Let a film of thickness d be in contact with vacuum along the plane $z=d$, and situated on a planar substrate at $z=0$ that is characterized by an impedance $\hat{Z}_0$. We will assume, for simplicity, that all fields are functions of only one coordinate in the planes parallel to the boundaries of the film, i.e., $\vec{E}(\vec{x};t)=\vec{E}(x,z;t)$, $\vec{H}(\vec{x};t)=\vec{H}(x,z;t)$. Then, in the case of p polarization, the components of the electric and magnetic fields in the film [denoted by a superscript (1)] at the boundary with the substrate are related by

$$E_x^{(1)}(k,\omega\,|\,0)=\hat{Z}_0 H_y^{(1)}(k,\omega\,|\,0) , \tag{1}$$

when a dependence of the components on x and t of the form $\exp(ikx-i\omega t)$ is assumed. Our aim is to investigate the dependence of the impedance of such a system,

$$\hat{Z}(k,\omega\,|\,d)=\frac{E_x^{(1)}(k,\omega\,|\,d)}{H_y^{(1)}(k,\omega\,|\,d)} , \tag{2}$$

on the film thickness d.

The frequency- and wave-vector-dependent dielectric constant of the dielectric film is assumed to be isotropic, and to have the form

$$\epsilon(\omega,\vec{k})=\epsilon_\infty \frac{\omega_\parallel^2+(\hbar\omega_\perp/m^*)k^2-\omega^2}{\omega_\perp^2-(\hbar\omega_\perp/m^*)k^2-\omega^2} , \tag{3}$$

where ϵ_∞ is the part of the dielectric constant that takes into account the contribution of all excitations whose frequencies are far from that of the exciton resonance being studied, m^* is the effective mass of the exciton responsible for the spatial dispersion, and $\omega_\parallel$ and $\omega_\perp$ are the frequencies of the longitudinal and transverse excitons at $\vec{k}=\vec{0}$.

The fields in the film are superpositions of the normal-mode fields and consequently can be written in the form

$$E_x^{(1)}(k,\omega\,|\,z)=\sum_j (E_j^{(\perp)}e^{\lambda_j z}+E_j^{(\parallel)}e^{\beta_j z}) , \tag{4}$$

$$H_y^{(1)}(k,\omega\,|\,z)=\sum_j \frac{i\omega\epsilon_j(\omega,k)}{c\lambda_j}E_j^{(\perp)}e^{\lambda_j z} . \tag{5}$$

Here the $\{\lambda_i\}$ are the (four) roots of the equation

$$k^2-\lambda^2=(\omega/c)^2\epsilon(\omega,k\hat{x}-i\lambda\hat{z}) , \tag{6a}$$

where $\hat{x}$ and $\hat{z}$ are unit vectors along the x and z axes, respectively, i.e.,

$$(k^2-\lambda_i^2)[Q_\perp^2(k)-\lambda_i^2]=\epsilon_\infty\frac{\omega^2}{c^2}[Q_\parallel^2(k)-\lambda_i^2] , \tag{6b}$$

and the $\{\beta_i\}$ are the (two) roots of the equation

$$\epsilon(\omega,k\hat{x}-i\beta\hat{z})=0 , \tag{7a}$$

i.e.,

$$\beta_i^2=Q_\parallel^2(k) , \tag{7b}$$

where

$$Q^2_{\parallel(\perp)}(k)=\frac{m^*}{\hbar\omega_\perp}(\omega^2_{\parallel(\perp)}-\omega^2)+k^2 . \tag{8}$$

We have also introduced, in Eq. (5), the notation

$$\epsilon_j(\omega,k)=\epsilon(\omega,k\hat{x}-i\lambda_j\hat{z}) . \tag{9}$$

The amplitudes $E_j^{(\perp)}$ and $E_j^{(\parallel)}$ are determined with the aid of the impedance boundary condition (1) on the plane $z=0$ and by additional boundary conditions that we assume to be of the form[1,2]

$$\alpha_i\vec{P}+\frac{\partial\vec{P}}{\partial n}=\vec{0} . \tag{10}$$

In these conditions $\vec{P}$ is the excitonic contribution to the polarization in the dielectric film,

$$\vec{P}(\vec{x},t)=\vec{P}(\vec{k},\omega)\exp(i\vec{k}\cdot\vec{x}-i\omega t) , \tag{11a}$$

$$\vec{P}(\vec{k},\omega)=\frac{1}{4\pi}[\epsilon(\omega,\vec{k})-\epsilon_\infty]\vec{E}(\vec{k},\omega) , \tag{11b}$$

and the α_i are certain constants that, in general, are different for the film-vacuum interface (α_1) and for the film-substrate interface (α_2); $\hat{n}$ is the outward normal to the boundary of the film. (Here, and in what follows, no account is taken of any "dead layer."[3,4])

For convenience, in the subsequent calculations we introduce the notation

$$\frac{1}{\lambda_i(Q_\perp^2-\lambda_i^2)}E_i^{(\perp)}=X_i . \tag{12}$$

In this notation Eqs. (10) assume the form

$$\sum_i[\alpha_1(q_\perp^2\lambda_iX_ie^{\lambda_id}-E_i^{(\parallel)}e^{\beta_id}) +(q_\perp^2\lambda_i^2X_ie^{\lambda_id}-\beta_iE_i^{(\parallel)}e^{\beta_id})]=0 , \tag{13}$$

$$\sum_i[\alpha_1(q_\perp^2k^2X_ie^{\lambda_id}-\beta_iE_i^{(\parallel)}e^{\beta_id}) +(k^2q_\perp^2\lambda_iX_ie^{\lambda_id}-\beta_i^2E_i^{(\parallel)}e^{\beta_id})]=0 , \tag{14}$$

$$\sum_i[\alpha_2(q_\perp^2\lambda_iX_i-E_i^{(\parallel)})-(q_\perp^2\lambda_i^2X_i-\beta_iE_i^{(\parallel)})]=0 , \tag{15}$$

$$\sum_i[\alpha_2(q_\perp^2k^2X_i-\beta_iE_i^{(\parallel)})-(q_\perp^2k^2\lambda_iX_i-\beta_i^2E_i^{(\parallel)})]=0 , \tag{16}$$

where we have set

$$\epsilon_i(\omega,k)-\epsilon_\infty=\epsilon_\infty\frac{Q_\parallel^2-\lambda_i^2}{Q_\perp^2-\lambda_i^2}-\epsilon_\infty=\epsilon_\infty\frac{Q_\parallel^2-Q_\perp^2}{Q_\perp^2-\lambda_i^2}\equiv\epsilon_\infty\frac{q_\perp^2}{Q_\perp^2-\lambda_i^2} , \tag{17}$$

while the boundary condition (1) becomes

$$\sum_i[X_i\lambda_i(Q_\perp^2-\lambda_i^2)+E_i^{(\parallel)}]=\hat{Z}_0\frac{i\omega}{c}\epsilon_\infty\sum_iX_i(Q_\parallel^2-\lambda_i^2) . \tag{18}$$

We thus have five equations for the six unknown amplitudes. Since it is relation (2) that interests us, we can make an arbitrary choice for the sixth equation, for example, the equation that results from setting the right-hand side of Eq. (18) equal to $\hat{Z}_0$.

Expressing $E_i^{(\parallel)}$, for example, through Eqs. (14) and (16), we obtain the following system of equations for the coefficients X_i:

$$\sum_iX_i(Q_\parallel^2-\lambda_i^2)=\frac{c}{i\omega\epsilon_\infty} , \tag{19}$$

$$\sum_iX_if_i=0 , \tag{20}$$

$$\sum_iX_ig_i=0 , \tag{21}$$

$$\sum_iX_iS_i=\hat{Z}_0 , \tag{22}$$

where

$$f_i=\lambda_i(\alpha_2-\lambda_i)+\frac{k^2}{W(Q_\parallel)}\{(\alpha_1+\lambda_i)(\alpha_2^2-Q_\parallel^2)e^{\lambda_id}-(\alpha_2-\lambda_i)[(\alpha_1\alpha_2+Q_\parallel^2)\cosh(Q_\parallel d)+Q_\parallel(\alpha_1+\alpha_2)\sinh(Q_\parallel d)]\} , \tag{23}$$

$$g_i=\lambda_i(\alpha_1+\lambda_i)e^{\lambda_id}+\frac{k^2}{W(Q_\parallel)}\{-(\alpha_2-\lambda_i)(\alpha_1^2-Q_\parallel^2)+(\alpha_1+\lambda_i)e^{\lambda_id}[(\alpha_1\alpha_2+Q_\parallel^2)\cosh(Q_\parallel d)+Q_\parallel(\alpha_1+\alpha_2)\sinh(Q_\parallel d)]\} , \tag{24}$$

$$S_i=\lambda_i(Q_\perp^2-\lambda_i^2)+\frac{k^2q_\perp^2}{W(Q_\parallel)}\{(\alpha_2-\lambda_i)[\alpha_1\cosh(Q_\parallel d)+Q_\parallel\sinh(Q_\parallel d)]-(\alpha_1+\lambda_i)\alpha_2e^{\lambda_id}\} , \tag{25}$$

$$W(Q_\parallel)=-Q_\parallel[(\alpha_1\alpha_2+Q_\parallel^2)\sinh(Q_\parallel d)+Q_\parallel(\alpha_1+\alpha_2)\cosh(Q_\parallel d)] . \tag{26}$$

The impedance $\hat{Z}(k,\omega\mid d)$ now takes the form

$$\hat{Z}(k,\omega\mid d)=\frac{\sum_iX_i\left[\lambda_i(Q_\perp^2-\lambda_i^2)e^{\lambda_id}+\frac{k^2q_\perp^2}{W(Q_\parallel)}\{\alpha_1(\alpha_2-\lambda_i)-(\alpha_1+\lambda_i)e^{\lambda_id}[\alpha_2\cosh(Q_\parallel d)+Q_\parallel\sinh(Q_\parallel d)]\}\right]}{\frac{i\omega}{c}\epsilon_\infty\sum_iX_i(Q_\parallel^2-\lambda_i^2)e^{\lambda_id}} . \tag{27}$$

The reflection coefficient for p-polarized light incident on the surface of the semiconducting film is given by the expression

$$|R|^2 = \left| \frac{\hat{Z}(k,\omega \mid d)+k_0}{\hat{Z}(k,\omega \mid d)-k_0} \right|^2 , \tag{28}$$

where $k_0=(\omega^2/c^2-k^2)^{1/2}=(\omega/c)\cos\theta$, with θ the angle of incidence.

We have calculated the reflection coefficient (28) for films of ZnSe of varying thickness deposited on an Al substrate. Two common forms of the additional boundary conditions (10) were used in these calculations. The first corresponds to $\alpha_1=\alpha_2=0$, viz.,

$$\frac{\partial \vec{P}}{\partial n}=\vec{0} , \tag{29a}$$

and has been used, e.g., in the work of Ting *et al.*[5] The second corresponds to $\alpha_1=\alpha_2=\infty$, viz.,

$$\vec{P}=\vec{0} , \tag{29b}$$

and is the additional boundary condition used by Pekar[6] in his original work on the effects of spatial dispersion on the optical properties of crystals.[7]

The parameters characterizing the ZnSe film were taken from the review by Koteles[8] and are

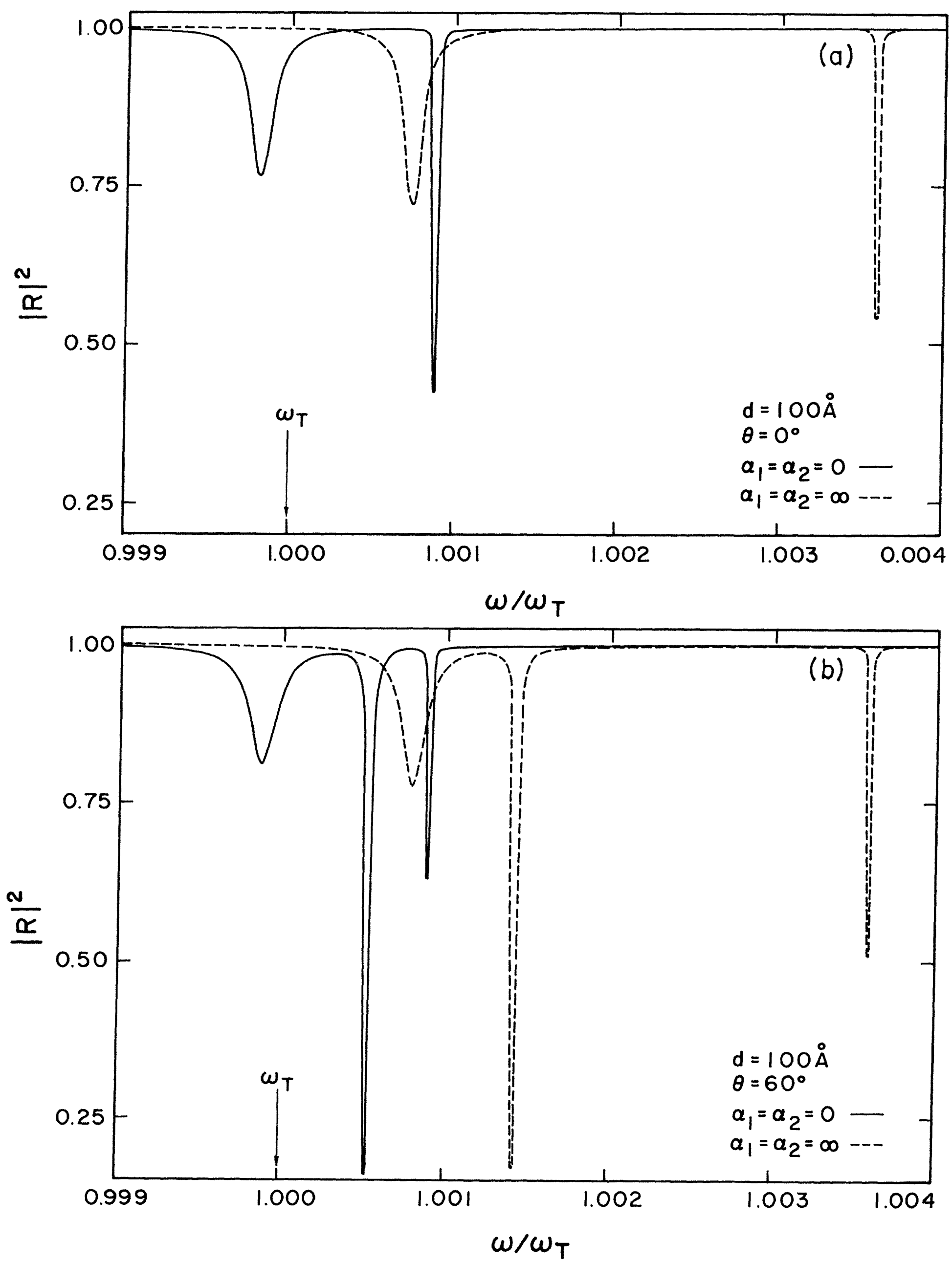

FIG. 1. Comparison of the reflection coefficients for a 100-Å-thick ZnSe film on an Al substrate obtained with the use of two different additional boundary conditions. (a) $\theta=0°$; (b) $\theta=60°$.

$$\epsilon_\infty = 8.7 \,,$$

$$\omega_T = 22\,602 \,,$$

$$\omega_L - \omega_T = 11.7 \,,$$

$$m^* = 1.49m \,,$$

with ω values measured in cm^{-1}. The surface impedance $\hat{Z}_0$ characterizing the metal-film interface at $z=0$ was taken to be of the form

$$\hat{Z}_0 = \frac{i}{|\epsilon(\omega)|^{1/2}} \,, \tag{30}$$

where $\epsilon(\omega)$, the dielectric constant of the metal, was assumed to have the free-electron form, $\epsilon(\omega) = 1 - \omega_p^2/\omega^2$, where the plasma frequency for the charge carriers in the bulk has the value $\omega_p = 120\,180$ cm^{-1} for aluminum.

In Fig. 1 we present our theoretical results for the frequency dependence of the reflection coefficient for a ZnSe film whose thickness is 100 Å. In Fig. 1(a) the results are shown for the case of normal incidence ($\theta = 0°$). In the case that $\alpha_1 = \alpha_2 = 0$, we see that the reflection coefficient contains two dips, one at $\omega/\omega_T = 0.999\,82$ and a second, narrower and deeper one at $\omega/\omega_T = 1.000\,88$. In the case that $\alpha_1 = \alpha_2 = \infty$ the reflection coefficient still has two dips, but their positions are shifted to higher frequencies in comparison with their positions when $\alpha_1 = \alpha_2 = 0$, viz., to $\omega/\omega_T = 1.000\,75$ and $\omega/\omega_T = 1.0036$. In Fig. 1(b) the reflection coefficient is plotted for an angle of incidence at 60°. It is seen that in this case the reflection coefficient has three dips for each of the two additional boundary conditions considered. The positions of the dips for $\alpha_1 = \alpha_2 = \infty$ are again shifted to higher frequencies with respect to their positions when $\alpha_1 = \alpha_2 = 0$. This shift of the resonant frequencies to higher values with increasing α_1 and α_2 is a general result that is discussed analytically in the Appendix for very thin films.

The results depicted in Figs. 1(a) and 1(b) differ not only quantitatively, viz., in the absolute positions of the reflectivity minima, but also qualitatively, in a way that should allow one to differentiate experimentally between the two additional boundary conditions used. We refer to the result that in the case that $\alpha_1 = \alpha_2 = 0$, one of the dips in the reflection coefficient lies below the frequency ω_T; in the case that $\alpha_1 = \alpha_2 = \infty$ all the dips in the reflection coefficient lie above the frequency ω_T.

As the thickness of the film increases the reflection coefficient acquires more dips that are associated with Fabry-Perot-type resonances in the film, and interferences between the several light waves present in the film. In Fig. 2 we present our results for ZnSe films of 500 Å thickness. It is seen that both in the case of normal incidence and in the case of oblique incidence both additional boundary conditions predict reflectivity minima below ω_T, so that the simple qualitative difference between the predictions of the two ABC's for very thin films discussed above is absent here.

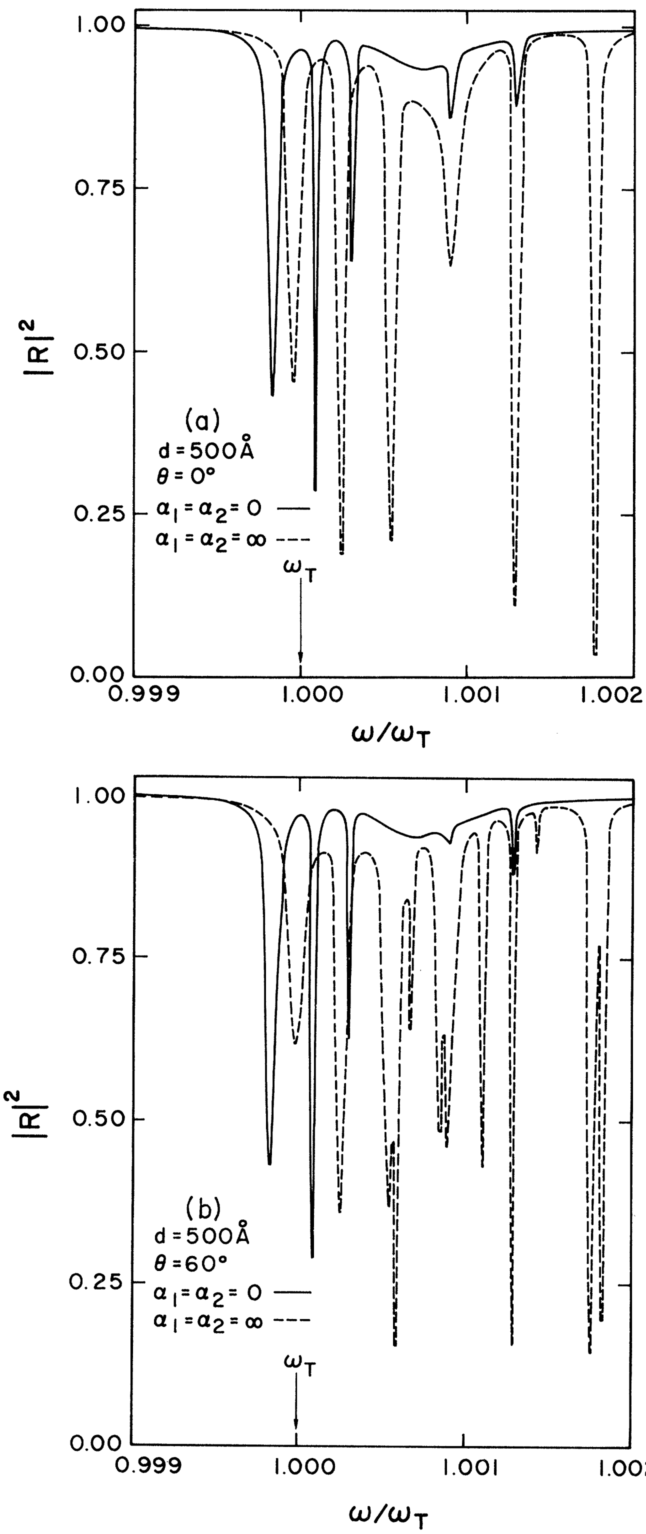

FIG. 2. The same as Fig. 1 except that the film thickness is 500 Å.

We note that the only adjustable parameters in this theory are the coefficients α_1 and α_2 in the boundary conditions (10), for which we have considered only two limiting sets of values in this paper. When experimental reflectivity data become available for the kind of thin film on a substrate system we have studied here, those data together with the theoretical expressions presented here can be used to obtain α_1 and α_2 from the best fit of theory to experiment. This can probably be done most easily in the limit of very thin films when the reflection coefficient has a particularly simple appearance, for which simple analytic expressions exist (see the Appendix). The presence of an additional variable parameter for a film not present in a semi-infinite medium, viz., its thickness, is of great significance in this kind of analysis.

Thus, since the optical properties of a thin film are determined by its impedance, while the form of the impedance depends very strongly on the form of the additional boundary conditions, investigation of the optical properties of thin films in the excitonic region of the spectrum could become, in our opinion, a rather simple way of determining the form of the additional boundary conditions.

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APPENDIX

The theoretical expressions obtained in the text are exact for the system studied in this paper. However, they are sufficiently complicated in form so that their properties are not readily discernible in the absence of numerical calculations.

In this appendix we obtain an approximate, analytic expression for the surface impedance of our system in the limit that the film thickness d satisfies the inequality $d \ll c/\omega n_i(\omega)$. While somewhat limited in its applicability, as we will see below, this approximate expression can nevertheless aid in the interpretation of the numerical results obtained in the text. It will be obtained by representing the effects of the film by an effective boundary condition at the plane $z=0$ that is exact to first order in d.

In this limit all components of the electromagnetic field change little across its thickness. Then, taking Maxwell's equations into account, we obtain for the fields in the film

$$E_x^{(1)}(x,d)=E_x^{(1)}(x,0)+d\left[\frac{\partial E_z^{(1)}}{\partial x}+\frac{i\omega}{c}H_y^{(1)}\right]_{z=0}, \tag{A1}$$

$$H_y^{(1)}(x,d)=H_y^{(1)}(x,0)+\frac{i\omega}{c}dD_x^{(1)}(x,0) \tag{A2}$$

to first order in the thickness d. To simplify the notation we have omitted explicit reference to the frequency dependence of the field components. The relations (A1) and (A2), together with the Maxwell boundary conditions $E_x^{(v)}(x,d)=E_x^{(1)}(x,d)$ and $H_y^{(v)}(x,d)=H_y^{(1)}(x,d)$, allow the field in the vacuum [denoted by a superscript (v)] at the interface with the film to be expressed in terms of the field in the film at the interface with the substrate.

With an accuracy through terms linear in d the fields $E_x^{(v)}(x,d)$ and $H_y^{(v)}(x,d)$ can be represented formally as

$$E_x^{(v)}(x,d)=E_x^{(v)}(x,0)+d\frac{\partial E_x^{(v)}}{\partial z}, \tag{A3}$$

$$H_y^{(v)}(x,d)=H_y^{(v)}(x,0)+d\frac{\partial H_y^{(v)}}{\partial z}. \tag{A4}$$

Expressing the derivatives with respect to z in Eqs. (A3) and (A4) in terms of derivatives with respect to x with the aid of Maxwell's equations, and taking into account the boundary condition $E_z^{(v)}(x,d)=D_z^{(1)}(x,d)$, as well as the continuity of H_y and E_x across the boundary $z=d$, we find that at $z=d$

$$\frac{\partial E_x^{(v)}}{\partial z}=\frac{\partial E_z^{(v)}}{\partial x}+\frac{i\omega}{c}H_y^{(v)}=\frac{\partial D_z^{(1)}}{\partial x}+\frac{i\omega}{c}H_y^{(1)}, \tag{A5}$$

$$\frac{\partial H_y^{(v)}}{\partial z}=\frac{i\omega}{c}E_x^{(v)}=\frac{i\omega}{c}E_x^{(1)}. \tag{A6}$$

As a result of Eqs. (A1)–(A6) we obtain

$$E_x^{(v)}(x,0)=E_x^{(1)}(x,0)+d\frac{\partial}{\partial x}(E_z^{(1)}-D_z^{(1)})_{z=0}, \tag{A7}$$

$$H_y^{(v)}(x,0)=H_y^{(1)}(x,0)+\frac{i\omega}{c}d(D_x^{(1)}-E_x^{(1)})_{z=0}. \tag{A8}$$

The difference $\vec{E}^{(1)}-\vec{D}^{(1)}$ can be expressed in terms of the excitonic part of the polarization $\vec{P}$ in the film[1]:

$$E_z^{(1)}-D_z^{(1)}=D_z^{(1)}\left[\frac{1}{\epsilon_\infty}-1\right]-\frac{4\pi}{\epsilon_\infty}P_z, \tag{A9}$$

$$D_x^{(1)}-E_x^{(1)}=(\epsilon_\infty-1)E_x^{(1)}+4\pi P_x. \tag{A10}$$

Making the replacements $D_z^{(1)}\cong E_z^v$, $E_x^{(1)}\cong E_x^v$, that are sufficiently accurate for our purposes, and eliminating $E_x^{(1)}(x,0)$ and $H_y^{(1)}(x,0)$ with the aid of Eq. (1), we obtain from Eqs. (A7)–(A10)

$$\left[1+\frac{i\omega}{c}d(\epsilon_\infty-1)\hat{Z}_0\right]E_x^{(v)}(x,0)=\hat{Z}_0H_y^{(v)}(x,0)+\frac{ic}{\omega}d\left[\frac{1}{\epsilon_\infty}-1\right]\frac{\partial^2H_y^{(v)}(x,0)}{\partial x^2}-\frac{4\pi}{\epsilon_\infty}d\frac{\partial P_z}{\partial x}-\frac{4\pi i\omega}{c}d\hat{Z}_0P_x. \tag{A11}$$

The result given by Eq. (A11) completely determines the impedance of the system, if the linear relations between P_z and $D_z^{(1)}\cong E_z^{(v)}$ and between P_x and $E_x^{(1)}\cong E_x^{(v)}$ are known.

We will assume that the exciton radius is much smaller than the thickness of the film. Therefore, in what follows we will use the bulk equations of motion of the polarization, assuming that appropriate additional boundary conditions are satisfied at the boundaries $z=0$ and $z=d$.

In the effective-mass approximation for an isotropic medium we have[1]

$$(\omega^2-\omega_{\parallel}^2)P_z+\frac{\hbar\omega_\perp}{m^*}\left[\frac{\partial^2P_z}{\partial x^2}+\frac{\partial^2P_z}{\partial z^2}\right]=-\frac{\omega_{\parallel}^2-\omega_\perp^2}{4\pi}D_z^{(1)}, \tag{A12}$$

$$(\omega^2-\omega_\perp^2)P_x+\frac{\hbar\omega_\perp}{m^*}\left[\frac{\partial^2P_x}{\partial x^2}+\frac{\partial^2P_x}{\partial z^2}\right]=-\frac{\omega_{\parallel}^2-\omega_\perp^2}{4\pi}\epsilon_\infty E_x^{(1)}. \tag{A13}$$

We note that although the polarization $\vec{P}$ varies slowly over the thickness of the film, the terms $\partial^2 P/\partial z^2$ in Eqs. (A12) and (A13) cannot be neglected. In fact, on integration over z from 0 to d these terms give the jump in the derivative $\partial\vec{P}/\partial z$ which, with the aid of Eq. (10), can be written in the form

$$\left.\frac{\partial\vec{P}}{\partial z}\right|_{z=d}-\left.\frac{\partial\vec{P}}{\partial z}\right|_{z=0}=-\alpha_1\vec{P}(x,d)-\alpha_2\vec{P}(x,0)$$

$$\cong-(\alpha_1+\alpha_2)\vec{P}(x,0)-\alpha_1\alpha_2 d\vec{P}(x,0)\ . \tag{A14}$$

Taking into account that in zero order with respect to d we can write $D_z^{(1)}\cong E_z^{(v)}=(ic/\omega)H_y^{(v)}$ and $E_x^{(1)}\cong E_x^{(v)}$, after integrating Eqs. (A12) and (A13) with respect to z with the aid of Eq. (A14) we have

$$\hat{L}_{\parallel}P_z(x)=\frac{cq_\perp^2}{4\pi i\omega}\frac{\partial H_y^{(v)}(x,0)}{\partial x}\ , \tag{A15}$$

$$\hat{L}_{\perp}P_x(x)=-\frac{\epsilon_\infty}{4\pi}q_\perp^2 E_x^{(v)}(x,0)\ , \tag{A16}$$

where

$$\hat{L}_{\parallel(\perp)}=\frac{d^2}{dx^2}-\kappa_{\parallel(\perp)}^2\ , \tag{A17}$$

$$\kappa_{\parallel(\perp)}^2=\frac{m^*}{\hbar\omega_\perp}(\tilde{\omega}_{\parallel(\perp)}^2-\omega^2)\ , \tag{A18}$$

$$\tilde{\omega}_{\parallel(\perp)}^2=\omega_{\parallel(\perp)}^2+\frac{\hbar\omega_\perp}{m^*}\left[\alpha_1\alpha_2+\frac{\alpha_1+\alpha_2}{d}\right]\ , \tag{A19}$$

$$q_\perp^2=\frac{m^*}{\hbar\omega_\perp}(\omega_\parallel^2-\omega_\perp^2)\ . \tag{A20}$$

Taking Fourier transforms of Eqs. (A11), (A15), and (A16), it is not difficult to obtain finally the impedance

$$\hat{Z}(k,\omega)=\frac{E_x^{(v)}(k)}{H_y^{(v)}(k)}=\frac{\hat{Z}_0+i(cd/\omega)k^2[1-\tilde{\epsilon}^{-1}(\omega,k)]}{1+i(\omega d/c)\hat{Z}_0[\tilde{\epsilon}(\omega,k)-1]}\ , \tag{A21}$$

where

$$\tilde{\epsilon}(\omega,k)=\epsilon_\infty\frac{\omega^2-\tilde{\omega}_\parallel^2-k^2\hbar\omega_\perp/m^*}{\omega^2-\tilde{\omega}_\perp^2-k^2\hbar\omega_\perp/m^*} \tag{A22}$$

is the effective dielectric permittivity of the film.

We note, first of all, that when $\alpha_1\to\infty$ and $\alpha_2\to\infty$ (which correspond to the Pekar[6] boundary condition), $\tilde{\epsilon}(\omega,k)\to\epsilon_\infty$ and the impedance assumes the form

$$\hat{Z}(\omega,k)=\frac{\hat{Z}_0+i(cd/\omega)k^2(1-\epsilon_\infty^{-1})}{1+i(\omega d/c)\hat{Z}_0(\epsilon_\infty-1)}\ . \tag{A23}$$

The impedance given by Eq. (A23) does not contain a contribution from the excitonic polarization, since in a sufficiently thin film the boundary condition $\vec{P}=\vec{0}$ leads to the vanishing of the excitonic polarization at each point in the

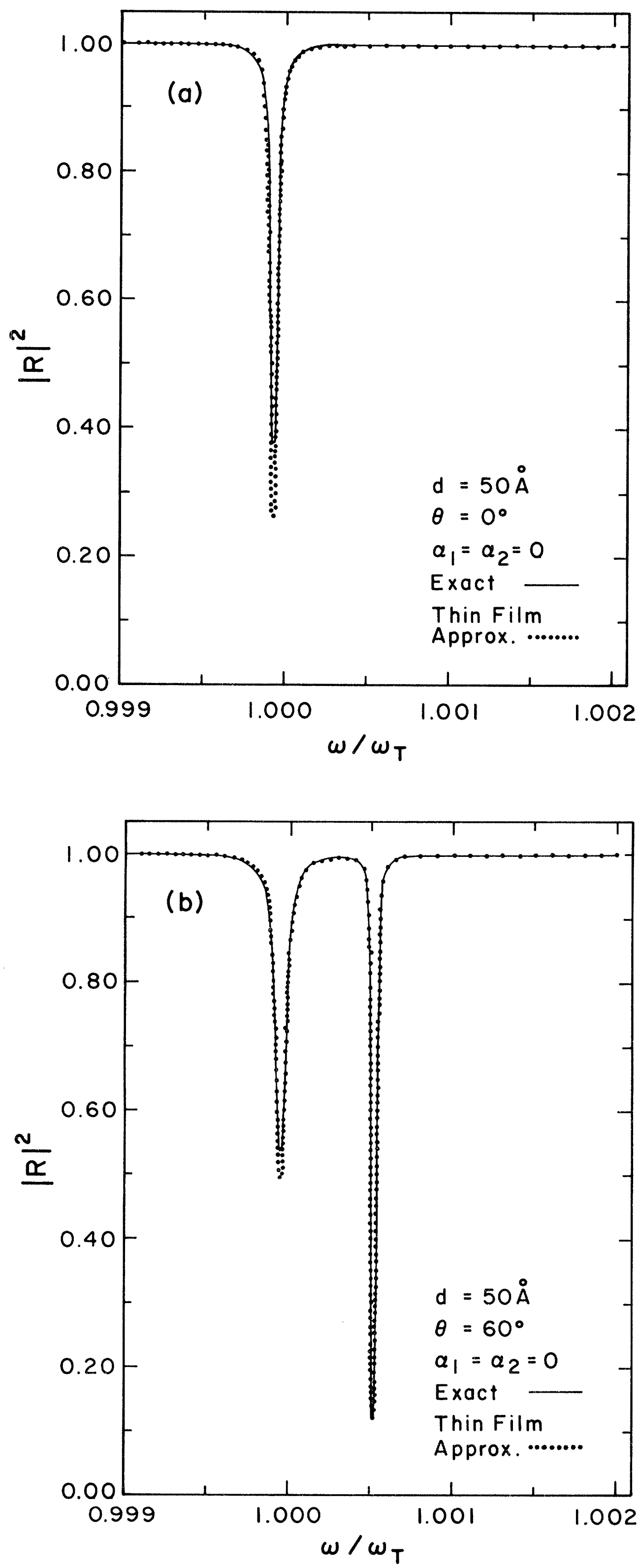

FIG. 3. Comparison of the reflection coefficients for a 50-Å-thick ZnSe film on an Al substrate in the case that $\alpha_1=\alpha_2=0$, obtained from the exact impedance, Eq. (27), and from the approximation valid for a very thin film, Eq. (A24). (a) $\theta=0°$; (b) $\theta=60°$.

film. The result that the approximate treatment presented in this appendix yields uninteresting results when the Pekar ABC's are used is perhaps the most severe limitation on its applicability.

On the other hand, if the additional boundary conditions have the form $\partial\vec{P}/\partial n=0$ ($\alpha_1=\alpha_2=0$),[5] then

$$\hat{Z}(\omega,k)=\frac{\hat{Z}_0+i(cd/\omega)k^2[1-\epsilon^{-1}(\omega,k)]}{1+i(\omega d/c)\hat{Z}_0[\epsilon(\omega,k)-1]}\ . \tag{A24}$$

In this case all the excitonic resonances are already manifested to first order in the film thickness d.

It is also easy to see that in the case of the mixed boundary conditions $P_z=0$, $\partial P_x/\partial z=0$,[9] only the resonance at the frequency of the transverse vibrations $\omega_\perp$ remains in the impedance, at the same time that for the boundary conditions $P_x=0$, $\partial P_z/\partial z=0$,[10] only the resonance at the frequency of the longitudinal vibrations manifests itself to first order in d.

In order to understand the "mechanism" by which the form of the additional boundary conditions influences the impedance of a thin semiconducting film, let us return to the general relation (A21). From the expression, Eq. (A22), for the dielectric permittivity $\tilde{\epsilon}(\omega,k)$ entering Eq. (A21) it follows that it corresponds to the bulk dielectric permittivity $\epsilon(\omega,k)$, but with shifted values of the resonance frequencies, viz.,

$$\begin{aligned}\tilde{\omega}_{\parallel}^2&=\omega_{\parallel}^2+\frac{\hbar\omega_\perp}{m^*}\left[\alpha_1\alpha_2+\frac{\alpha_1+\alpha_2}{d}\right],\\ \tilde{\omega}_{\perp}^2&=\omega_{\perp}^2+\frac{\hbar\omega_\perp}{m^*}\left[\alpha_1\alpha_2+\frac{\alpha_1+\alpha_2}{d}\right].\end{aligned} \tag{A25}$$

For sufficiently large values of the α_i, as can be seen from Eqs. (A25), the shift in the resonance frequencies becomes anomalously large, and the entire semiconducting film (under the influence of the additional boundary conditions) in fact goes over into a "dead-layer" state.

This reason for the creation of a dead layer differs significantly from the one considered in Ref. 4, inasmuch as in our case the thickness of the film is assumed to be large compared with the Bohr radius of the exciton.

We emphasize also that the shift in the resonance frequency found in this work (its lowering in the case of a positive effective mass) has a different mechanism from the one studied in Ref. 11, since in that work the thickness of the film was considered to be small in comparison with the Bohr radius.

These results are illustrated in Fig. 3, where the reflectivity of a 50-Å-thick ZnSe film on an aluminum substrate calculated from Eq. (A24) is plotted for two different angles of incidence. For comparison the reflectivity calculated on the basis of the exact result for the surface impedance, Eq. (27), when $\alpha_1=\alpha_2=0$ is also plotted in this figure. The exact result predicts reflectivity minima that are not quite as deep as those obtained from the approximate expression, but the agreement between the positions of the minima and their widths obtained from the two different calculations has to be regarded as excellent. When the thickness of the film is doubled to 100 Å this good agreement is already lost.

It appears as if the simple theory of the impedance of a thin film on a substrate presented in this appendix describes well the results of the exact calculations for those resonances for which the corresponding electromagnetic field in the film is smoothly varying. However, in a sufficiently thin film, with increasing α_1 and α_2 the resonance shifts in frequency and at the same time the amplitude of the rapidly varying part of the field grows. Therefore, at some values of α_1 and α_2 the present approximate theory ceases to be valid.

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