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Resonant scattering of light by excitonic rough surfaces

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The Rayleigh-Fano approach is used to study the scattering of p-polarized light from the deterministically shaped rough surface of a semiconductor in the vicinity of an isolated excitonic transition. Nonlocal effects are accounted by the Hopfield and Thomas dielectric function. A perturbative formalism is developed to calculate the amplitudes of the scattered fields up to second order on the roughness height. Numerical results are presented for the $A_{n=1}$ excitonic transition of CdS using different choices of additional boundary conditions. Comparisons are made with the local model calculations and discussed in terms of resonant elastic scattering. The differential reflectance spectra peaks are also shown and interpreted as surface-exciton-polariton coupling.

I. INTRODUCTION

The enhancement of electromagnetic fields near rough surfaces has been an interesting subject in the past few years. Since the resonant enhancement depends critically on the surface shape, many experimental studies have been performed on the detection of the scattered light from metals[1–3] and excitonic semiconductors[4] with nonflat surfaces. Local[5–11] and nonlocal[4,12,13] theories have been developed to calculate the amplitudes of scattered fields near inhomogeneous boundaries.

The macroscopic dielectric response of a solid may be frequency dependent, $\epsilon(\omega)$, or wave-vector dependent as well, $\epsilon(\omega, \mathbf{q})$. The theory describing the former case is said to be local, while in the latter case is termed nonlocal. Here, we are concerned with the nonlocal theory as we consider the polarizability of the medium due to excitons. Nonlocal or spatial dispersion effects have been introduced in the theory of optics for semiconductor materials by the Hopfield and Thomas[14] excitonic dielectric function $\epsilon(\omega, \mathbf{q})$. This is a classical model of coupled harmonic oscillators, which takes into account the center of mass motion of the exciton. Using the excitonic dielectric function $\epsilon(\omega, \mathbf{q})$ in the electromagnetic dispersion relations of the longitudinal and transverse waves, one finds three solutions[14] for the wave vector $\mathbf{q} = (Q, 0, q)$, of which one is longitudinal and two are transverse. The additional modes, to those appearing in local optics, propagate in the semiconductor and are unaffected by each other in the bulk, although they may couple at the surface. Due to the multitude of scattered waves at the surface, the Maxwell boundary conditions are insufficient to determine all the amplitudes of the fields. Therefore, additional boundary conditions[14–23] (ABC's) are needed.

In recent years Sel'kin and co-workers[4,16] have measured the scattered light from randomly rough semiconductor surfaces. Their studies were focused on the exciton resonances and the problem of the ABC equations. The measured scattered cross sections were compared with the theoretical calculations[4] using the Pekar[15] boundary conditions and a first order perturbation approach. Studies of flat surfaces have led these authors to argue that the boundary conditions depend critically on surface sample preparation and because of this fact, they have reformulated[16] the ABC equations. In the search of the appropriate ABC equations, we believe that investigations of the surface exciton polariton resonant scattering of light from deterministic rough surfaces and the direct comparisons of the diffraction spectra with the experimental measurements will determine the suitable boundary conditions.

In this paper we study the ABC problem for the deterministic rough surface of a semiconductor in the vicinity of an isolated excitonic transition. We present a perturbative theory for the scattering of light by a spatially dispersive medium neglecting any effects of the exciton-free dead layer. The scattered amplitudes of the electromagnetic fields are calculated up to second order on the height of the surface roughness with generalized[17] ABC equations in the absence of surface currents. Our formalism is general within the frame of the Rayleigh-Fano[13] approach, and we exemplify its use by solving a sinusoidal grating. We compare the results of the differential reflectance using two ABC's with the local calculations and discuss them in terms of the surface-exciton-polariton coupling. We also consider the attenuated total reflectivity spectra of the surface modes excitation.

II. THEORY

We consider the plane of incidence to be the xz plane, and the surface profile to be defined by

$$f(x,z) \equiv z + h\xi(x) = 0, \tag{1}$$

where h is the roughness height and $\xi(x)$ is the surface profile. The unit vector $\mathbf{n}(\xi)$ directed normally outward from the surface is

$$\mathbf{n}(\xi) = \frac{\nabla f}{|\nabla f|} = \frac{(-h\xi_x, 0, -1)}{[(h\xi_x)^2 + 1]^{1/2}}, \quad (2)$$

where $\xi_x = \partial\xi(x)/\partial x$, and the outward normal derivative of $\mathbf{n}$ is

$$\frac{\partial}{\partial \mathbf{n}} = -\mathbf{n} \cdot \nabla. \quad (3)$$

We assume that the excitonic semiconductor fills the $z > -h\xi(x)$ space and is characterized by the Hopfield and Thomas[14] dielectric response

$$\epsilon(\omega, \mathbf{q}) = \epsilon_0 + \frac{\omega_p^2}{\omega_T^2 - \omega^2 + Dq^2 - i\omega\nu}, \quad (4)$$

where ϵ_0 is the background dielectric constant, ω_p is a measure of the oscillator strength, ω_T is the frequency of the excitonic transition, ν is a phenomenological damping parameter, $\mathbf{q}$ is the wave vector, and $D = \hbar\omega_T/(m_e + m_h)$, where m_e and m_h are the electron and hole masses, respectively. For the region $z < -h\xi(x)$ we consider vacuum.

Since excitonic waves are allowed to propagate in the semiconductor, for the p-polarized (the electric field $\mathbf{E}$ is on the plane of incidence) light considered here, there are a total of three modes with wave vector $\mathbf{q} = (Q, 0, q)$. Two of them are transverse waves that satisfy the dispersion relations $\mathbf{q}_n^2 = (\omega^2/c^2)\epsilon(\omega, \mathbf{q}_n)$, $n = 1, 2$, and the third one is a longitudinal wave with dispersion relation $\epsilon(\omega, \mathbf{q}_3) = 0$. The amplitudes of the scattered light can be calculated using the Maxwell boundary conditions together with the ABC equations at the surface profile.

The well-known Maxwell boundary conditions are the continuity of the tangential projections of the electric field $\mathbf{E}(\mathbf{r}, t)$ and the magnetic field $\mathbf{H}(\mathbf{r}, t) = \mathbf{B}(\mathbf{r}, t)$, which can be cast into the forms

$$\mathbf{E} - (\mathbf{n} \cdot \mathbf{E})\mathbf{n} \quad \text{and} \quad \mathbf{B} - (\mathbf{n} \cdot \mathbf{B})\mathbf{n}. \quad (5)$$

In our work we use the Agranovich ABC equations[17]

$$\underline{B}_2\mathbf{P} + \frac{\partial \mathbf{P}}{\partial \mathbf{n}} = 0, \quad (6)$$

where $\underline{B}_2 = \mathrm{diag}(\alpha, \alpha)$, with α being a parameter, complex in general.

The x component of $\mathbf{E}(\mathbf{r}, t)$ for the incident, reflected and transmitted waves has the following forms. The incident field is given by

$$E_{xI}(\mathbf{r}, t) = E_{xI}(Q_I)e^{i(Q_I x + q_I z - \omega t)}, \quad (7)$$

with $Q_I^2 + q_I^2 = \omega^2/c^2$. The reflected field is given by

$$E_{xr}(\mathbf{r}, t) = \sum_Q E_x(Q)e^{i(Qx - qz - \omega t)}, \quad (8)$$

with $Q^2 + q^2 = \omega^2/c^2$. And the transmitted field is given by

$$E_{xt}(\mathbf{r}, t) = \sum_{n=1}^{3}\sum_Q E_n(Q)e^{i(Qx + q_n z - \omega t)}, \quad (9)$$

where q_n are the components of the wave vector for the transverse and longitudinal modes in the semiconductor. The corresponding magnetic fields are calculated[18] from the Maxwell equation $\nabla \times \mathbf{E} = -(1/c)\partial\mathbf{B}/\partial t$. The excitonic polarization vector is given by[18]

$$\mathbf{P}(\mathbf{r}, t) = \frac{\omega_p^2}{4\pi D}\sum_{n=1}^{3}\sum_Q X_n(Q)\mathbf{E}_n(Q)e^{i(Qx + q_n z - \omega t)}, \quad (10)$$

where we have defined $X_n(Q) = 1/[q_n^2(Q) - \Gamma^2]$ and $\Gamma^2 = (\omega^2 - \omega_T^2 - Dq^2 + i\omega\nu)/D$.

Application of the Maxwell boundary conditions and the x and z components of the ABC equations [Eq. (6)] at the surface allows one to write the following matrix equation for the scattered amplitudes:

$$\sum_Q \mathbf{R}(Q, x)\mathbf{T}(Q, x)\mathbf{A}(Q)e^{iQx} = \mathbf{I}(Q_I, x)e^{iQ_I x}, \quad (11)$$

where

$$\mathbf{R}(Q, x) = \begin{pmatrix} a & a_1 & a_2 & a_3 \\ Y(Q) & -Y_1(Q) & -Y_2(Q) & 0 \\ 0 & b_1X_1(Q) & b_2X_2(Q) & b_3X_3(Q) \\ 0 & D_1(Q)b_1X_1(Q) & D_2(Q)b_2X_2(Q) & D_3(Q)b_3X_3(Q) \end{pmatrix}, \quad (12)$$

$$\mathbf{T}(Q, x) = \mathrm{diag}\left(e^{-i(q+q_I)z_0}, e^{i(q_1-q_I)z_0}, e^{-i(q_2-q_I)z_0}, e^{-i(q_3-q_I)z_0}\right), \quad (13)$$

$$\mathbf{A}(Q) = \begin{pmatrix} E_x(Q) \\ E_1(Q) \\ E_2(Q) \\ E_3(Q) \end{pmatrix}, \quad (14)$$

and

$$\mathbf{I}(Q_I, x) = \begin{pmatrix} a_I \\ -Y_I \\ 0 \\ 0 \end{pmatrix} E_{xI}(Q_I), \quad (15)$$

with $Y(Q) = \omega/cq(Q)$, $Y_I = Y(Q_I)$, $Y_n(Q) = \omega\epsilon_n(Q)/cq_n(Q)$, $D_n(Q) = Q/q_n(Q)$, $n = 1,2$, $D_3(Q) = -q_3(Q)/Q$, $a_I = a(Q_I)$, and

$$a = a(Q,x) = 1 - (n_x^2 - n_x n_z Q/q), \tag{16}$$

$$a_n = a_n(Q,x) = 1 - (n_x^2 - n_x n_z Q/q_n),\ n = 1,2, \tag{17}$$

$$a_3 = a_3(Q,x) = 1 - (n_x^2 + n_x n_z q_3/Q), \tag{18}$$

$$b_n = b_n(Q,x) = \alpha - \frac{i(h\xi_x Q + q_n)}{(1 + h^2\xi_x^2)^{1/2}},\ n = 1,2,3, \tag{19}$$

where $n_x(n_z)$ is the $x(z)$ component of $\mathbf{n}$.

We use a perturbative approach similar to that of Ref. 13 and apply the solution to a sinusoidal grating $\xi(x) = \sin(gx)$. We find that the first order fields have only nonspecular contributions with $Q = Q_I \pm g$ while the second order has contributions of the specular dispersion with $Q = Q_I$ and nonspecular ones with $Q = Q_I \pm 2g$.

III. RESULTS AND DISCUSSION

We present numerical results of the scattered amplitudes of the electromagnetic fields up to second order on h for the grating of CdS in the vicinity of the $A_{n=1}$ excitonic transition. We report two limiting cases of ABC equations: $\alpha = \infty$ and $\alpha = 0$, corresponding to the Pekar[15] ($\mathbf{P} = 0$) and Ting, Frankel, and Birman[19] ($\partial_n \mathbf{P} = 0$) boundary conditions, respectively. We focus our attention on the scattered fields with the x component of the wave vector $Q = Q_I$ for the zeroth order, $Q = Q_I \pm g$ for the first order, and for $Q = Q_I$ for the second order. The numerical values of the parameters are $\hbar\omega_T = 2.552$ eV, $\nu = 10^{-6}\omega_T$, $\omega_p = 0.11517\omega_T$, $\epsilon_0 = 9.1$, and $D = 6.17 \times 10^{-5}c^2$.

The enhancement factors are defined for the first order terms by

$$R_1^{\pm} = \frac{1}{g}\frac{|E_x^{(1)}(Q_I \pm g)|}{|E_{xI}(Q_I)|}, \tag{20}$$

and for the second order term by

$$R_2 = \frac{1}{g^2}\frac{|E_x^{(2)}(Q_I)|}{|E_{xI}(Q_I)|}, \tag{21}$$

where we have introduced the expansion $\mathbf{E} = \sum_n h^n \mathbf{E}^{(n)}$.

We now describe the results. We start by discussing the scattered fields when the frequency of the incident light is fixed and the wave vector $g = 2\pi/\lambda_g$ of the profile is varied. The scattered amplitudes to first order R_1^+ are shown in Fig. 1 for an angle of incidence of $\theta = 10°$ and a frequency of $\omega/\omega_T = 1.0005$. We compare two nonlocal cases, the Pekar and Ting, Frankel, and Birman conditions, with the local one. The nonlocal calculations as well as local spectrum have surface-exciton resonant scattering, indicated by SM^+, at $Q = Q_I + g$ whenever R_0 has poles.[13] (The corresponding expression R_1^- for scattering at $Q = Q_I - g$ will be denoted by SM^- in the following figures.) It is seen that at this frequency the Ting, Frankel, and Birman condition gives nearly the same spectrum as the local one. On the other hand, the Pekar condition spectrum shows a less prominent resonant peak with a small shift in g.

The second order enhancement amplitudes R_2 are presented in Fig. 2 for $\theta = 10^o$ and $\omega/\omega_T = 1.0005$. R_2 has two nonspecular resonances at $Q = Q_I \pm g$, indicated in the figure by $SM^{\pm}$, due to surface exciton polariton coupling. It is apparent that the Ting, Frankel, and Birman condition and the local curves have similar behavior with sharp peaks, while the Pekar case exhibits less prominent peaks.

We now turn to show the enhancement factors as functions of the frequency ω/ω_T for fixed values of cg/ω_T. In Fig. 3 we present results of the first order fields for $cg/\omega_T = 1.9$ and $\theta = 50°$. The figure displays R_1^+ with the two ABC's and the dispersionless case. We indicate the surface mode resonance by SM^+. The two curves with spatial dispersion effects exhibit a res-

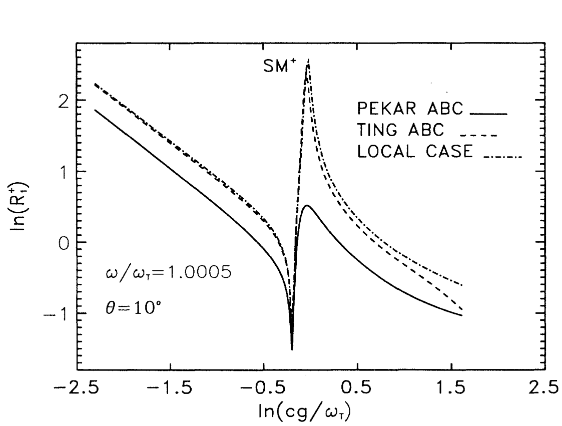

FIG. 1. First order enhancement factors R_1^+ as function of g, of the scattered fields from a CdS sinusoidal profile in the vicinity of the $A_{n=1}$ excitonic transition with the Ting, Frankel, and Birman (Ref. 19) ABC ($\partial_n \mathbf{P} = 0$), the Pekar (Ref. 15) ABC ($\mathbf{P} = 0$), and the local case. The angle of incidence θ is 10° and ω/ω_T is 1.0005.

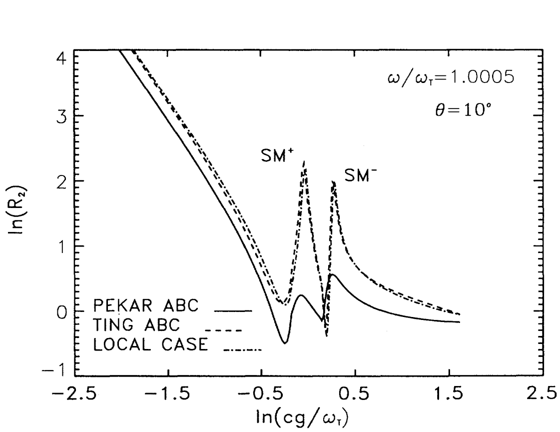

FIG. 2. Second order enhancement factors R_2 as function of g with the Ting, Frankel, and Birman (Ref. 19) ABC, the Pekar (Ref. 15) ABC, and the local case, for $\theta = 10°$ and $\omega/\omega_T = 1.0005$.

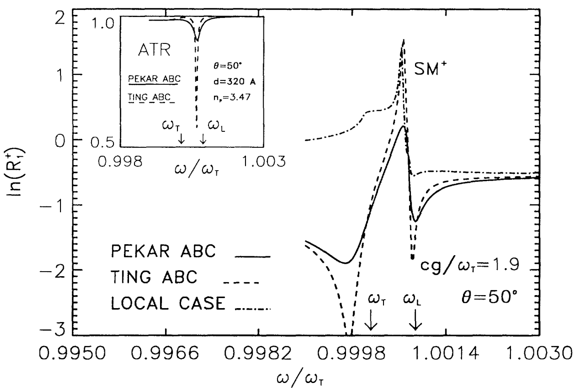

FIG. 3. First order enhancement factors R_1^+ as function of ω with the Ting, Frankel, and Birman (Ref. 19) ABC, the Pekar (Ref. 15) ABC, and the local case, for $cg/\omega_T = 1.9$ and $\theta = 50°$. In the inset we show the ATR spectra from a flat CdS surface with the prism index of refraction $n_p = 3.47$, the gap thickness $d = 320$ Å, in order to compare with the frequency location of the resonant surface exciton coupling.

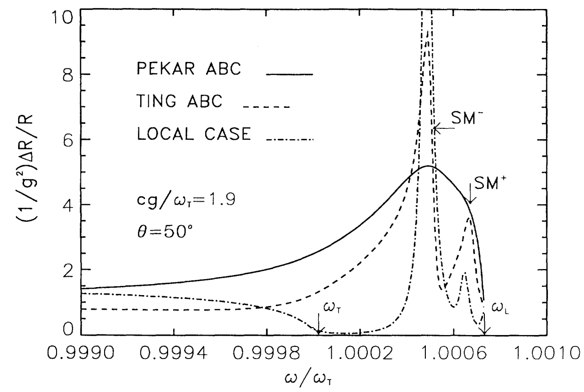

FIG. 5. Differential reflectance of p-polarized light incident at an angle $\theta = 50°$ and $cg/\omega_T = 1.9$. Two ABC's are considered and compared with the local model calculations.

onant peak at the same frequency, but have different strength. The dispersionless curve shows a resonant peak at nearly the same frequency but is shifted to lower frequencies, a small spike at the longitudinal exciton frequency $\omega_L = (\omega_T^2 + \omega_p^2/\epsilon_0)^{1/2} = 1.000\,73\omega_T$ and a shoulder at the excitonic transition ω_T. In the inset we present results of the attenuated total reflectivity[24] (ATR) of a flat CdS surface using the Pekar and Ting, Frankel, and Birman ABC's. For this, we consider the peak frequency of the scattered fields and choose the parameters in such a way that the parallel component of the wave vector of the surface wave is equal to the Q of Fig. 3. To achieve this, we consider an angle of incidence of $\theta = 50°$ and a coupling prism of index of refraction $n_p = 3.47$. The air gap thickness is $d = 320$ Å. By looking at the position of the peak of the scattered light (SM^+) and the reflectivity minima, it is noticed that they take place at the same

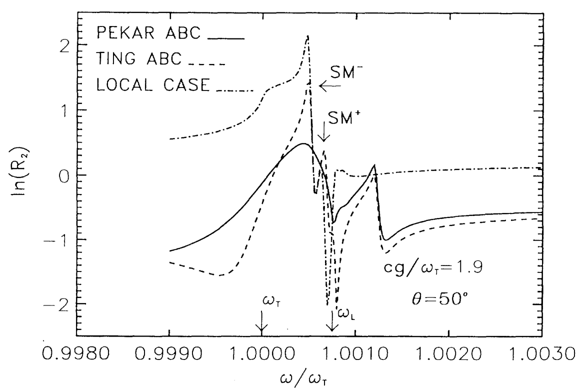

FIG. 4. Second order enhancement factors R_2 as function of ω with the Ting, Frankel, and Birman (Ref. 19) ABC, the Pekar (Ref. 15) ABC, and the local case, for $cg/\omega_T = 1.9$ and $\theta = 50°$.

frequency. Since the calculations show well-defined scattering peaks, the surface exciton polariton excitation can be achieved experimentally by suitable periodic surface profile preparation.

The effects of different choices of ABC equations on the second order fields are displayed in Fig. 4, where we plot R_2 as functions of the frequency for $\theta = 50°$ and $cg/\omega_T = 1.9$. The spectrum for the Ting, Frankel, and Birman ABC shows two well-defined peaks between ω_T and ω_L, which correspond to the coupling of light with the surface exciton modes and are indicated by SM^- and SM^+. The local case shows similar structure as the Ting, Frankel, and Birman case. On the other hand, the Pekar case exhibits a maximum at SM^- and a very small shoulder at SM^+.

The changes in the normalized reflectance $\Delta R/R = 2Re(E^{(2)}/E^{(0)})$ for p-polarized light as functions of the frequency ω/ω_T are shown in Fig. 5 for a rough surface with $gc/\omega_T = 1.9$ and $\theta = 50^o$. We compare the results using two ABC's with the local model calculations. The structures in this figure are closely correlated to the second order calculations shown in Fig. 4. The resonant peaks are indicated by $SM^{\pm}$. The Ting, Frankel, and Birman condition and the local case show the two peaks of the surface excitons, while the Pekar case exhibits only a maximum at the frequency of SM^- and a shoulder at the frequency of SM^+. From this figure we see that the direct comparisons with experimental measurements could determine a better choice of additional boundary conditions for excitonic systems.

IV. CONCLUSIONS

We have developed a perturbative formalism, up to second order, to study light scattering from a deterministically shaped rough surface of a semiconductor in the vicinity of an isolated excitonic transition, taking into account spatial dispersion effects. Numerical results have been presented for the exciton $A_{n=1}$ of CdS using the Rayleigh-Fano approach and two choices of boundary conditions, namely, the Pekar and Ting, Frankel, and

Birman ABC equations. In the case of the variation of λ_g, the fact that the second order peaks are at $Q = Q_I \pm g$ where the first order peaks appear, and are nearly at the same Q value for the local case, allows one to interpret the structure as surface mode resonances. As functions of frequency, the spectra exhibit rich structure, which is interpreted as surface exciton resonances between ω_T and ω_L. We have also reported the attenuated total reflectivity minima of surface modes coupling. Since the roughness of deterministic shaped surface contributes additional wave vector g to the incident light providing well-defined scattering peaks, an alternative experimental method is suggested for surface exciton polariton studies. Using two ABC's, we also show that the differential reflectance exhibits peaks of the surface exciton coupling with the incident light. We anticipate that the future comparisons with the experimental data will allow one to choose the best suited boundary equations to include the nonlocal excitonic effects.

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