Modeling the Optical Constants of Diamond- and Zincblende-Type Semiconductors: Discrete and Continuum Exciton Effects at $E_0$ and $E_1$

F.H. Pollak1), M. Muñoz2), T. Holden, K. Wei, and V. M. Asnin

Physics Department and NY State Center for Advanced Technology in Ultrafast Photonic Materials and Applications, Brooklyn College of CUNY, Brooklyn, NY 11210, USA

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We present a comprehensive model dielectric function $\varepsilon(E) = \varepsilon_1 + i\varepsilon_2$ for diamond- and zincblende-type semiconductors based on the energy-band structure near critical points (CPs) plus discrete as well as continuum excitonic effects at the $E_0$, $E_0 + \Delta_0$, $E_1$, and $E_1 + \Delta_1$ CPs. In addition to the energies of these band-to-band CPs, our analysis also yields information about the binding energies of not only the 3D exciton associated with $E_0$ ($R_0$), when resolved, but also the 2D exciton related to the $E_1$, $E_1 + \Delta_1$ CPs ($R_1$). This model has been applied to spectral ellipsometry measurements of $\varepsilon_1$, $\varepsilon_2$ (0.3 eV < $E$ < 5.5 eV) of ZnCdSe/InP, CdTe$_{1-x}$S$_x$, In$_{0.66}$Ga$_{0.34}$As, and GaSb and a surface photovoltage spectroscopy determination of the absorption coefficient of GaAs near $E_0$. This work shows conclusively that even if the exciton at $E_0$ is not resolved the lineshape is continuum exciton. The obtained values of $R_1$ exhibit a trend which is in good agreement with effective mass $k \cdot p$ theory. Our analysis will be compared with the modeling of Adachi and the University of Illinois-Chicago group, both of whom neglect exciton continuum effects and hence have not evaluated $R_1$. Our results, particularly for exciton continuum effects at $E_1$, have considerable implications for recent first-principles band structure calculations which include exciton effects.

The optical constants associated with electronic transitions of diamond- and-zincblende-type (DZB) materials have been measured by a number of methods. During the past decade spectral ellipsometry (SE) has been used by number of investigators including Aspnes and Studna [1], Cardona and coworkers [2,3], Adachi and coworkers [4], the University of Illinois-Chicago group [5], etc. However, these workers either did not model the optical constants [1 to 3] or used an incomplete single particle expression [4, 5]. Cardona and coworkers fit derivative (with respect to photon energy) spectra employing a two-dimensional density of states for the “$E_1$, $E_1 + \Delta_1$” features; exciton effects were taken into account by means of a phase angle (Slater-Koster “contact” potential) [2,3]. Recently, Holden et al. [6] have presented a comprehensive model dielectric function $\varepsilon(E) = \varepsilon_1 + i\varepsilon_2$ for DZB semiconductors based on the energy-band structure near critical points (CPs) plus discrete as well as band-to-band Coulomb enhanced (BBCE) effects, i.e., continuum excitons, at the $E_0$, $E_0 + \Delta_0$, $E_1$, and $E_1 + \Delta_1$ CPs. In addition to the energies of these band-to-band CPs, this analysis also yields information about the binding energies of not only the 3D exciton associated with

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1) Corresponding author: Tel.: 718/951-5356; Fax: 718/951-4871; e-mail: FHPCBC@CUNYVM.CUNY.EDU
2) Permanent address: Departamento de Fisica, CINVESTAV, Mexico DF, Mexico. e-mail: MARTIN@FIS.CINVESTAV.MX
When resolved, but also the 2D exciton related to the $E_1$, $E_1 + \Delta_1$ CPs ($R_1$). This model has already been applied to SE measurements of $\varepsilon_1$, $\varepsilon_2$ (energy range $0.3 \text{ eV} < E < 5.5 \text{ eV}$) of ZnCdSe/InP [6], CdTe$_{1-x}$S$_x$ [7], and In$_{0.66}$Ga$_{0.34}$As (undoped as well as n- and p-doped) [8].

In this paper we present an SE investigation of GaSb (in the photon energy range 0.3 to 5.3 eV) as well as a surface photovoltage spectroscopy (SPS) study of undoped GaAs near $E_0$. By fitting the SE data of GaSb to the Holden model we have evaluated $R_1$ in addition to the energies of the various CPs. The values of $R_1$ for ZnCdSe/InP, CdS, CdTe, In$_{0.66}$Ga$_{0.34}$As, and GaSb exhibit a trend which is in good agreement with effective mass/k·p theory [9]. The ability to determine $R_1$ has considerable implications for recent first-principles band structure calculations which include exciton effects [10]. An analysis of the GaAs SPS data (measured in this work) and the CdTe SE [8] results near $E_0$ show conclusively that even if the exciton at this CP is not resolved the line-shape is BBCE and not band-to-band single particle (BBSP) [4,5].

The sample consisted of bulk GaSb (001) (cut 4° towards [110]). The optical data in the range 0.75 to 5.3 eV were taken using an Instruments SA variable angle ellipsometer while for the interval 0.3 to 0.8 eV a variable angle instrument which used a Fourier transform infrared reflectometer as a light source was employed. Thus there was some overlap between the two intervals. The SPS data were taken using a normalized Kelvin probe technique [11].

The solid line in Fig. 1 is the experimental imaginary component $\varepsilon_2(E)$ of the complex dielectric function for GaSb. The obtained $\varepsilon_1(E)$ spectrum is presented in Ref. [12]. Our data are very similar to that ones reported in Refs. [1,2,13] in the appropriate energy ranges. References [1,2] made measurements only in the range 1.5 to 5.5 eV. There is an absorption edge around 0.7 eV, doublet peaks in the range 2.0 to 2.5 eV.

![Fig. 1. The solid and dashed lines represent the experimental and fit values, respectively, of the imaginary component ($\varepsilon_2$) of the complex dielectric function of GaSb](image-url)
and a large feature with a peak around 4 eV with some structure on the low energy side around 3.5 eV. There is also a weak feature at around 1.5 eV, not observed in Refs. [1,2,13].

The data of Fig. 1 near the \( E_0 \) band gap has been fit to a function which contains Lorentzian broadened (a) discrete excitonic (DE) and (b) 3D \( M_0 \) BBCE contributions, i.e., continuum exciton effects. As will be demonstrated below, even if the \( E_0 \) exciton is not resolved, the Coulomb interaction still affects the band-to-band lineshape. Therefore we can write [6 to 8, 12]

\[
e_{2}(E) = \text{Im} \left\{ \frac{A}{E^2} \left\{ \frac{2R_0}{(E_0 - R_0) - E - i\Gamma_0} + \frac{2R_0}{(E_0 - R_0) + E + i\Gamma_0} \right\} \\ + \left\{ \frac{\theta(E' - E_0)}{1 - e^{-2\pi\gamma_1(E')}} - \frac{\theta(-E' - E_0)}{1 - e^{-2\pi\gamma_2(E')}} \right\} \frac{d'E}{E' - E - i\Gamma} \right\},
\]

where \( A \) is a constant, \( E_0 \) is the energy of the direct gap, \( R_0 \) is the effective Rydberg energy \([= (E_0 - E_0^\text{ex})]\), \( \Gamma_0^\text{ex} \) is the broadening of the exciton, \( \Gamma_0 \) is the broadening parameter for the BBCE transition, \( \gamma_1(E) = [R_0/(E_0 - E_0^\text{ex})]^{1/2} \), \( \gamma_2(E) = [R_0/(-E - E_0)]^{1/2} \) and \( \theta(x) \) is the unit step function. For the \( E_0 + \Delta_0 \) transition, Eq. (1) will have \( A \to B \), \( E_0 \to E_0 + \Delta_0 \), \( R_0 \to R_{so} \) and \( \Gamma \to \Gamma_{so} \).

For \( E_1 \) we use [6 to 8, 12]

\[
e_{2}(E) = \text{Im} \left\{ \frac{C_1}{E^2} \left\{ \frac{4R_1}{(E_1 - R_1) - E - i\Gamma_{E_1}} + \frac{4R_1}{(E_1 - R_1) + E + i\Gamma_{E_1}} \right\} \\ + \left\{ \frac{\theta(E' - E_1)}{1 + e^{-2\pi\gamma_3(E')}} - \frac{\theta(-E' - E_1)}{1 + e^{-2\pi\gamma_4(E')}} \right\} \frac{d'E}{E' - E - i\Gamma_{E_1}} \right\},
\]

where \( C_1 \) is a constant, \( E_1 \) is the energy of the gap, \( R_1 \) is the 2D Rydberg energy, \( \Gamma_{E_1} \) is the broadening parameter for both the exciton and band-to-band transition, \( \gamma_3(E) = [R_1/4(E - E_1)]^{1/2} \), and \( \gamma_4(E) = [R_1/4(-E - E_1)]^{1/2} \). For the \( E_1 + \Delta_1 \) CP, Eq. (2) has \( C_1 \to C_2 \) and \( E_1 \to E_1 + \Delta_1 \), \( \Gamma_{E_1} \to \Gamma_{E_1 + \Delta_1} \), etc. The same 2D Rydberg \( (R_1) \) was used for both \( E_1 \) and \( E_1 + \Delta_1 \) CP features.

Because of their complexity, the \( E_0', E_0' + \Delta_0' \), and \( E_2 \) features each have been described by a damped harmonic oscillator term [6 to 8, 12]. The fact that Ref. [10] has found that \( E_2 \), like the \( E_0' / E_0 + \Delta_0 \) and \( E_1 / E_1 + \Delta_1 \) CP features, contains an excitonic component provides some justification in using a damped oscillator term for this feature.

Shown by the dotted curve in Fig. 1 is the fit to the experimental data using the above expressions. Since the exciton at \( E_0 / E_0 + \Delta_0 \) is not resolved we have taken \( R_0 (= 1.6 \text{ meV}) \) from Ref. [14]. Because of the large number of fitting parameters, values for the various gaps and their broadening parameters were initialized from values obtained by numerically taking the first-derivative of the dielectric functions with respect to energy. The details of this approach are given in Refs. [6 to 8, 12]. The final obtained values of the various energies are indicated by arrows in the figures. All relevant parameters are listed in Ref. [12]. Our values of the various energy gaps, i.e., \( E_0, E_0 + \Delta_0, E_1 - R_1, (E_1 + \Delta_1) - R_1 \), etc. are in good agreement with other works [1,2,13,14].
It is important to note that due to the relatively large values of $R_1$ ($\approx 30$ to $300$ meV), as listed in Table 1, the optical structure associated with the $E_1$, $E_1 + \Delta_1$ CPs in DZB semiconductors are actually mainly the excitonic features $E_1 \pm \pm R_1$, $(E_1 + \Delta_1) \pm \pm R_1$, respectively, as denoted in Fig. 1. Almost all prior optical [1 to 5] and modulated (see, for example, [15]) optical studies have incorrectly labelled these excitonic features as “$E_1$, $E_1 + \Delta_1$”.

Our value of $R_1$ ($32 \pm 3$ meV) is in fairly good agreement with the effective mass/ $k \cdot p$ theory of Ref. [9]. According to the approach

$$R_1 \propto \mu_\perp / \varepsilon_1^2(\infty),$$

where $\mu_\perp$ is the perpendicular reduced interband effective mass and $\varepsilon_1(\infty)$ is the high frequency dielectric function. This calculation yields $R_1 = 25$ meV, as listed in Table 1.

Table 1 also presents the experimental and calculated values of $R_1$ for several materials. The latter are based on the theory of Ref. [9]. The experimental numbers for $R_1$ exhibit a trend which is in good agreement with effective mass/ $k \cdot p$ theory. More reliable theoretical values can now be obtained from the recent first-principles band structure calculations which include exciton effects [10].

The solid lines in Fig. 2a and b are the experimental values of the numerical derivatives $d\varepsilon_2/dE$ for CdTe and $d\alpha/dE$ for GaAs, respectively, where $\alpha$ is the absorption coefficient. The former is from Ref. [8] while the latter is our SPS study. It has been shown that the SPS data in the vicinity of $E_0$ are proportional to $\alpha$ (see, for example, [11]). Both lineshapes are approximately Lorentzian with a slight asymmetric broadening on the high energy side. This indicates that the DE is not resolved since the first-derivative of its Lorentzian lineshape would produce an “S” shaped component. The dotted lines in Fig. 2 are least-square fits to an analytical form for the first derivative of Eq. (1), as given in Ref. [6], where $\Gamma_0^{ex}$ has been taken sufficiently large so that the DE is not resolved. The obtained values of $E_0$ are indicated by arrows. The dashed lines are fits to the first-derivative of a BBSP profile, i.e., $\text{Im} (E - E_0 + i\Gamma_0)^{-1/2}$. This produces a very asymmetric lineshape which does not fit the experimental data very well.

In Ref. [6] the DE at $E_0$ was well resolved and it was evident that the band-to-band lineshape was BBCE and not BBSP. The results of Fig. 2 clearly demonstrate that even if the DE is not resolved the lineshape is the former and not the latter, an expression

<table>
<thead>
<tr>
<th>Material</th>
<th>Experiment $R_1$ (meV)</th>
<th>Effective mass/ $k \cdot p$ theory $R_1$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.53}$Cd$</em>{0.47}$Se/InP</td>
<td>270 ± 50$^a$</td>
<td>300</td>
</tr>
<tr>
<td>CdS</td>
<td>205 ± 30$^b$</td>
<td>290</td>
</tr>
<tr>
<td>CdTe</td>
<td>145 ± 50$^b$</td>
<td>150</td>
</tr>
<tr>
<td>In$<em>{0.66}$Ga$</em>{0.34}$As</td>
<td>92 ± 15$^c$</td>
<td>55</td>
</tr>
<tr>
<td>GaSb</td>
<td>32 ± 3$^d$</td>
<td>25</td>
</tr>
</tbody>
</table>

$^a$) Ref. [6].
$^b$) Ref. [8].
$^c$) Ref. [7].
$^d$) This work and Ref. [12].
that has been incorrectly employed in Refs. [4,5]. Also because Adachi and coworkers and the University of Illinois-Chicago group used a BBSP expression at $E_1$ they were not able to extract $R_1$.

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**References**

Note added in proof: We have also recently evaluated and fit the optical constants of two samples of Ga$_{1-x}$In$_x$As$_y$Sb$_{1-y}$/GaSb ($x \approx 0.16$, $y \approx 0.14$). We find $R_1 = 30 \pm 5$ meV (experiment) and 26 meV (effective mass/k \cdot p theory) [M. Muñoz, K. Wei, F.H. Pollak, J.L. Freeouf, C.A. Wang, and G.W. Charache, submitted to J. Appl. Phys.].