# Photoreflectance line shape of excitonic transitions analyzed with a redefined set of fitting parameters

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We analyze experimental and simulated photoreflectance spectra of excitonic transitions in semiconductors with a redefined set of fitting parameters in Aspnes' line shape function. The redefinition, based on a comparison with the first derivative of a Gaussian, allows one to directly relate these parameters to the observed experimental spectrum, making them independent of the exponent $m$. None of the original information, including the underlying physics involved as determined by $m$, is lost in this process. The physical significance of the fitting parameters is explained. Their usefulness lie in making line shape fitting easier and the possibility of comparing different sets of samples exhibiting inhomogeneities with regard to their broadening, oscillator strengths, and hence, quality. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1379051]

Photoreflectance (PR) spectroscopy has emerged as an important tool for both the study and the postgrowth characterization of semiconductor quantum structures and devices based on them.[1–3] In PR, a modulated laser beam is used to generate photoexcited carriers, which modify an existing built-in electric field inside the structure resulting in a modulation of its dielectric function $\epsilon$. The energy dependence of the change, i.e., $\Delta\epsilon$, is then studied by measuring the relative change in the sample's reflectance $[\Delta R/R(E)]$ using a second beam of variable energy $(E)$. $|\Delta\epsilon|$ exhibits a maximum at energies near a critical point in the sample's electronic band structure and results in sharp, derivative-like features in the $\Delta R/R(E)$ spectrum at these energies. By fitting an appropriate line shape function to this experimental spectrum, one obtains parameters, which give information on the sample's electronic band structure and properties dependent on it. This information is extremely useful for characterization, therefore line shape functions have received much attention in the literature.[4–7] For an excitonic transition, the PR spectrum is first-derivative like[7] and, if it is Lorentzian broadened (LB), the spectrum is best approximated by Aspnes' line shape function[4]

$$\frac{\Delta R}{R}(E) = \Re e\left[\frac{Ae^{i\Theta}}{(E-E_0+i\Gamma)^m}\right] \tag{1}$$

with the exponent $m=2$. The fitting parameter $E_0$ represents the transition energy, and the broadening $\Gamma$ is proportional to the inverse of the exciton lifetime. In the absence of interference effects, the phase $\Theta$ indicates the mechanism of $\epsilon$ modulation.[7] The amplitude $A$ is related to the exciton oscillator strength and the extent of modulation.

In high quality samples, however, exciton-phonon coupling at high temperatures leads to Gaussian-broadened exciton transitions (GBET)[8] as also do inhomogeneities such as composition and thickness fluctuation in quantum wells (QW). The line shape function for such cases is complicated, requiring the use of degenerate hypergeometric functions, but it is known that Eq. (1) approximates such line shapes well for $m=3$. In addition, $m=2.5$ is required to fit a nonexcitonic band-to-band (BB) transition at a $M_0$ critical point under low built-in electric field conditions. However, varying $m$ leads to significant changes in the values of the fitting parameters $\Gamma$, $A$, and $\Theta$. An example is shown in Fig. 1(a), where the experimental PR spectrum of the transition at the fundamental gap of an epitaxial InP film is fitted with Eq. (1) for different $m$. The values of the fitting parameters (set A) thus obtained are listed in Table I. Note that the value of $A$ is not directly related to the experimental $\Delta R/R$ amplitude. This is not ideal for practical material characterization. For example, when studying the temperature dependence of line shapes in QWs,[7] the use of $m=3$ (GBET at high temperature) and $m=2$ (LB at low-temperatures) results in abrupt changes in the parameter values. Similarly, when characterizing a set of epitaxial samples of different quality, where some of them are good enough to have excitonic transitions (thereby requiring $m=2$ or 3 for fitting), while others are not (therefore $m=2.5$ is required, representing BB transitions), the use of the appropriate $m$ for different samples would result in sets of parameters that are not directly comparable. Moreover, nonlinear-least-squares curve-fitting routines require a good estimate of the initial values of the fitting parameters in order to achieve convergence.[9] Since there is no direct $m$ independent correlation between the experimental data and these fitting parameters, a quick good guess for initial values is difficult to make. From a characterization point of view, it would be better, if one could use the appropriate $m$ as required by the physics and, in addition, obtain values of fitting parameters that do not change with $m$ and can be simply related to the experimental spectrum. In order to achieve this, we define a set of fitting parameters in the following.

We considered a normalized Gaussian of full width at half maximum (FWHM) $\sigma$:

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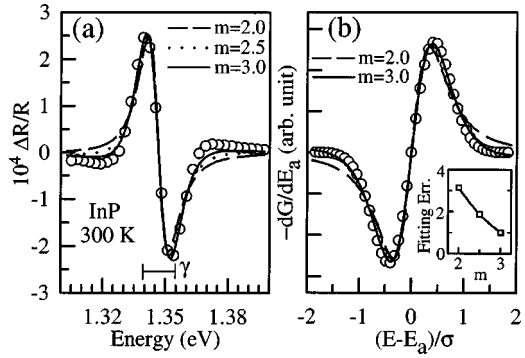


FIG. 1. (a) Experimental PR spectrum (○) of InP fitted with Eq. (1) for different $m$ as indicated. (b) Calculated (○) $dG/dE_a$ and fits with Eq. (1) (lines) for $m=2$ and 3. Inset: root-mean-squared curve-fitting error for different $m$ (relative to $m=3$).

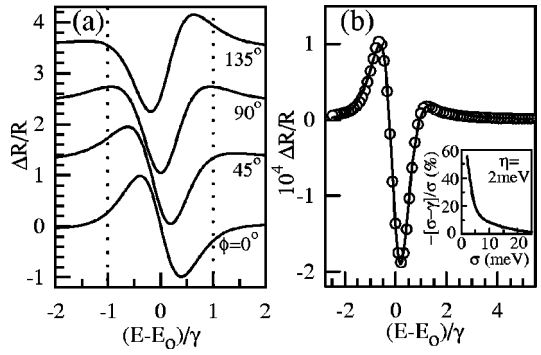


FIG. 2. (a) Line shape symmetry for different $\phi$ with $m=3$ and $a=1$, the plots (vertically displaced) can be inverted by adding 180° to $\phi$. (b) Typical simulated (circles) PR spectrum of a GaAs (5 nm)/$Al_{0.3}Ga_{0.7}As$ (20 nm) QW ground state GBET fitted with Eq. (3) using $m=3$ (line). The main parameters in the simulation were $f=7\times10^{14}$ m$^{-2}$, $\Delta E_0=410$ $\mu$eV, $\eta=2$ meV, and $\sigma=10$ meV, while $\gamma=10.8$ meV was obtained from fitting. Inset: difference between $\sigma$ in simulations and $\gamma$ obtained from fitting.

$$G(E)=\frac{1}{\sqrt{\pi}\sigma'}\exp\left[-\frac{(E-E_a)^2}{\sigma'^2}\right], \tag{2}$$

where $\sigma'=\sigma/\sqrt{4\ln(2)}$. Taking a clue from the fact that excitonic transitions in PR are first-derivative like, we fit $dG/dE_a$ in the energy range $|E-E_a|\leqslant 2\sigma$ with Eq. (1) for $m=2$, 2.5, and 3. The best and worst fit are shown in Fig. 1(b). We found that $\Gamma$ is related to $\sigma$ for different $m$ by $\Gamma\simeq\kappa_1\sigma$, where $\kappa_1=0.364m-0.147$. We therefore replaced $\Gamma$ by $\kappa_1\gamma$, thus defining a broadening parameter $\gamma$, which approximately equals $\sigma$. Next, to take into account the dependence of the amplitude parameter[4] on $\Gamma$ and $m$, we replaced $A$ by $a\kappa_2(\kappa_1\gamma)^m$. The extra factor $\kappa_2=-0.115m+1.7$, also obtained through fitting makes the amplitude parameter $a$ approximately equal to the amplitude of $dG/dE_a$. Since the relation between $\gamma$ and $\sigma$ as well as $a$ and amplitude of $dG/dE_a$ were obtained empirically through fitting, it is important to determine the errors involved in these approximations. We find that the errors are less than 0.2% in both cases. Note that for $m=3$, we have $\kappa_1=0.945$ so that $\gamma\simeq\Gamma$. Also with $m=3$, one obtains the minimum root-mean-squared curve-fitting error [inset of Fig. 1(b)]. This demonstrates that $m=3$ best suits a GBET, because it represents the member of the set of generalized Lorentzians in Eq. (1) (in the range $2\leqslant m\leqslant 3$), which is the closest approximation to the first energy derivative of a Gaussian. Finally, taking into account the $m$ dependence[4] of $\Theta$, we replaced it by $\phi+(m-3)\times(\pi/2)$.

TABLE I. Parameter values (original and redefined set) obtained by fitting the InP spectrum with Eqs. (1) and (3).

| Set A $m$ | $E_0$ (eV) | $\Gamma$ (meV) | $A$ (eV$^m$) | $\Theta$ (°) | Fit error |
|---|---|---|---|---|---|
| 2.0 | 1.346 | 8.4 | $2.5\times10^{-8}$ | 261 | $2.3\times10^{-6}$ |
| 2.5 | 1.346 | 11.2 | $4.6\times10^{-9}$ | 307 | $1.6\times10^{-6}$ |
| 3.0 | 1.346 | 14.0 | $9.1\times10^{-10}$ | 352 | $1.0\times10^{-6}$ |
| Set B $m$ | $E_0$ (eV) | $\gamma$ (meV) | $a(10^{-4})$ | $\phi$(°) | Fit error |
| 2.0 | 1.346 | 14.5 | 2.4 | 351 | $2.3\times10^{-6}$ |
| 2.5 | 1.346 | 14.7 | 2.4 | 352 | $1.6\times10^{-6}$ |
| 3.0 | 1.346 | 14.8 | 2.4 | 352 | $1.0\times10^{-6}$ |

With the redefined fitting parameters, the line shape function becomes

$$\frac{\Delta R}{R}(E)=\Re e\left[\frac{a\kappa_2(\kappa_1\gamma)^m e^{i[\phi+[m-3](\pi/2)]}}{(E-E_0+i\kappa_1\gamma)^m}\right]. \tag{3}$$

The values of the parameters ($\gamma$, $a$, and $\phi$) do not change much with $m$ when fitting the InP spectrum (set B, Table I). With both sets of parameters, the fitting error in Table I is the same for a given $m$ and minimal for $m=3$ suggesting that this spectral feature arises from a GBET. A specific value of $A$, $\Gamma$, and $\Theta$ for a particular $m$ has physical significance in that they describe the appropriate dielectric function and modulation mechanism. However, this information is not lost because, if we know the appropriate $m$, we can easily obtain the values $\Gamma[=\kappa_1\gamma]$, and $\Theta[=\phi+(m-3)(\pi/2)]$. Thus, none of the underlying physical information associated with the old set of parameters is lost. The value of $a$ is now directly comparable to the $\Delta R/R$ amplitude. Figure 2(a) shows how the symmetry of the line shapes vary as a function of $\phi$. Their basic symmetry is independent of $m$ in the range $2\leqslant m\leqslant 3$. Comparing the experimental spectrum to such a plot, it is easy to make a good guess for the initial values of $E_0$, $\gamma$, $a$, and $\phi$ for fitting.

Next we consider the physical significance of the new parameters. The interpretation of $\phi$ remains similar to $\Theta$ for excitonic transitions, as long as interference effects are negligible and the Seraphin coefficients[10] $\alpha$ and $\beta$ can be approximated as being constant and 0, respectively. Under these conditions, when $\phi=90°$ or 270° (phase shift by 180° corresponding to sign reversal), the mechanism for $\epsilon$ modulation is the shift of the exciton energy. Similarly, $\phi=0°$ or 180° indicates a mechanism related to broadening and/or oscillator strength change for $\epsilon$ modulation. To determine the significance of $\gamma$ and $a$, we studied their values obtained from fitting a simulated PR spectrum of the ground-state

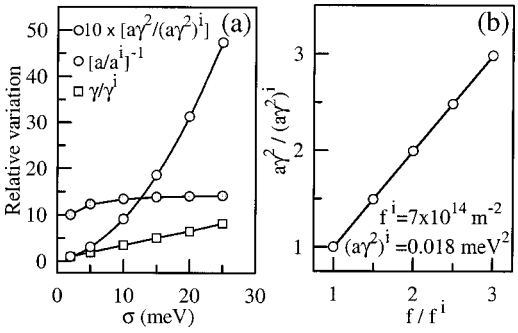


FIG. 3. (a) Relative variation of $a$, $\gamma$, and $a\gamma^2$ obtained from fitting, as $\sigma$ is changed in the simulations. Note that the $a\gamma^2$ variation is amplified by a factor of 10. Initial values (denoted with superscript $i$) were $\gamma^i=3.1$ meV and $a^i=1.4\times10^{-3}$ at $\sigma=2$ meV. All lines are to guide the eye. (b) The linear variation of $a\gamma^2$ obtained from fitting as a function of $f$ in the simulations (with $\sigma=10$ meV).

exciton transition in a GaAs/(Al,Ga)As QW as a general example, in the simulations, we first considered a QW exciton dielectric function $\epsilon$ of the form[11]

$$\epsilon(E)=\epsilon_\infty+\frac{fe^2\hbar^2}{\mu\epsilon_0 L_z}\frac{I}{(E_0^2-E^2-i\eta E)}, \tag{4}$$

where $E_0$, $f$, $\mu$, $L_z$, and $\eta$ denote the transition energy, oscillator strength (per unit area), reduced mass, QW width, and homogeneous linewidth (2 meV), respectively. Next, to account for a larger inhomogeneous broadening due to $L_z$ and/or composition fluctuations, we considered a distribution of $E_0$ values with a weight factor for averaging the dielectric function given by a normalized Gaussian distribution with FWHM$=\sigma$. The reflectivity was calculated using the transfer matrix approach.[12] The values of the required material parameters were obtained either directly from or by comparing the simulated spectrum with those in the literature. $\Delta R$ was calculated by considering that the dominant contribution to the change in $\epsilon$ arises from a shift $\Delta E_0$ in $E_0$ via the quantum-confined Stark effect.[7,13–15]

Figure 2(b) shows an example of a simulated spectrum fitted with Eq. (3). A study of the relationship between $\gamma$ obtained from fitting simulations with different $\sigma$ [inset of Fig. 2(b)] shows that for exciton dominated line shapes $\gamma\simeq\sigma$, when $\sigma\gg\eta$. Thus, when inhomogeneities lead to a GBET transition, $\gamma$ is a good estimate of the width of the distribution of transition energies, and from it one can estimate the extent of inhomogeneities such as $L_z$ and/or composition distributions in QWs. For a normalized Gaussian, $|(dG/dE_a)_{E=E_a\pm\sigma/2}|\sigma^2$ is a constant. By analogy, we might expect that in the low-field PR spectrum of QW $a\gamma^2$ would be constant. Figure 3(a) shows that, although $a$ and $\gamma$ change significantly as $\sigma$ is varied, $a\gamma^2$ [magnified $\times10$ in Fig. 3(a)] remains nearly constant. The simulation and fitting study also shows that $a\gamma^2$ is proportional to the oscillator strength $f$ (and also to $\Delta E_0$, the modulation induced shift in the exciton transition energy) as indicated by the linear relationship in Fig. 3(b). This suggests that studying the variation of $a\gamma^2$ can be useful for characterization purposes. For example, the values of $a\gamma^2$ for a series of similar QW samples would reflect their relative $f$ and, hence, an aspect of the sample quality. The relative variation in $f$ as a function of temperature can also be studied in this fashion by accounting for the temperature dependent change in linewidths. Similarly, the variation of $a\gamma^2$ as a function of pump beam intensity in PR can be used to study relative changes in $\Delta E_0$.

In conclusion, we have studied PR lineshapes of excitonic transitions using a set of redefined fitting parameters in Aspnes' line shape function. We find that the values of the new parameters relate directly to the experimental spectrum independently of the exponent $m$ in the range $2\leqslant m\leqslant3$, while retaining all the physical information contained in the original parameters. This makes the equation easy to use for fitting and enables comparison of spectral features relative to the first derivative of a Gaussian. For GBETs resulting from inhomogeneities, the additional information that one obtains from these parameters should be useful for characterization purposes.

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