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Applied Surface Science 212–213 (2003) 782–786
applied surface science
www.elsevier.com/locate/apsusc

# Surface-induced broadening and shift of exciton resonances in the thin film regime

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**Abstract**

We derive and analyze the relaxation frequency $\nu$ and the shift $\Delta\omega$ of excitonic resonances in the regime of weak confinement (also known as thin film regime). In calculating $\nu$ and $\Delta\omega$, we have solved the integral equation for the averaged Green's function within the self-consistent Born approximation. The dependencies of $\nu$ and $\Delta\omega$ on the parameters of the excitonic thin film and its rough interfaces are found. We present specific results for CuCl, where the thin film regime is maintained up to a very small sample thickness.


*PACS:* 71.35.-y; 78.66.-w

*Keywords:* Excitons; Thin films; Surface roughness; Inhomogeneous broadening

## 1. Introduction

Excitons in confined systems are the focus of attention of many research groups because of their intriguing optical properties and the potential applications to optoelectronic devices. There exist two qualitatively different regimes of exciton confinement: strong and weak confinement regimes, which are determined by the ratio between the characteristic size of the confinement region and the exciton Bohr radius $a_0$. In the regime of strong exciton confinement (or quantum well regime), the thickness of the quantum well $d$ is smaller than the exciton radius $a_0$ ($d \leq a_0$). Here, the Coulomb attraction between the electron and hole is suppressed in the growth direction because of the dominant effect of the confining potential on their motion perpendicular to the quantum-well plane. Due to the in-plane Coulomb interaction, the electron–hole pair in a quantum well forms a quasi-2D exciton. In the opposite case ($d \gg a_0$, thin film regime), the relative motion of the electron–hole pair is practically the same as in the bulk except for a small distortion near film boundaries, which gives rise to exciton-free layers. Consequently, the center-of-mass motion of the exciton turns out to be quantized in an effective length $d_{eff}$ smaller than the actual film thickness $d$ ($d_{eff} \approx d - 2l$, $l$ is the effective size of one exciton-free layer) [1–3].

It is noteworthy that for materials such as CuCl, which is characterized by excitons with a large binding energy (~190 meV) and a very small radius $a_0 \sim 7$ Å, the thin film regime can be maintained up to a rather small thickness of the order of a few

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0169-4332/03/$ – see front matter 
doi:10.1016/S0169-4332(03)00102-8

nanometers. Besides, the exciton-free layers in CuCl are quite narrow ($l \sim a_0$) and, consequently, their presence does not affect, in fact, the optical spectra (reflectivity, transmission, absorption) [4–6]. Therefore, CuCl has turned out to be a very useful material for studying the exciton center-of-mass quantization in very thin films [7,8].

The behavior of excitons in CuCl thin films has been mostly investigated by assuming that the thin-film interfaces are ideally flat. However, realistic structures of thin films have inherent roughness, which produces fluctuations in the exciton center-of-mass confining potential and, consequently, a considerable increase of the inhomogeneous broadening $\nu$ as well as the shift $\Delta\omega$ of the excitonic resonances. In the few works [4–8], where the effect of scattering between exciton and interface disorder on optical spectra for very thin films was taken into account, models for $\nu$ and $\Delta\omega$, without any strict derivation, were employed.

The aim of the present work is to calculate systematically both the coefficient of inhomogeneous broadening $\nu$ and the shift $\Delta\omega$ of exciton resonances, associated with the interface roughness of very thin films. The calculation will be based on the application of the self-consistent Green's function method (Section 2). In Section 3, we will present numerical results for CuCl thin films.

## 2. Formulation of the problem

Let us consider a semiconductor thin film, which occupies the space $\xi(x) \le z \le d$, where $z$ is the coordinate along the growth direction. The function $\xi(x)$ is a zero-mean, stationary, random process, determined by the standard properties

$$\langle \xi(x) \rangle = 0, \qquad \langle \xi(x)\xi(x') \rangle = \zeta^2 W(|x - x'|). \qquad (1)$$

The angular brackets indicate an average over the ensemble of realizations of the function $\xi(x)$, $\zeta$ is the characteristic deviation from the average surface $z = 0$. The correlator $W(|x|)$ has unit amplitude, $W(0) = 1$, and a typical scale $R_c$ of monotonous decrease. According to our geometry, the lower boundary of the film is assumed to be randomly rough while the upper one is, for simplicity, flat. Nevertheless, such a system is physically equivalent to a film with both boundaries being rough, statistically identical, and not intercorrelated [9].

We shall consider a semiconductor characterized by an exciton with very small radius ($a_0 \ll d$, $a_0 \ll R_c$). In this case, the effective length $d_{eff}$, where the exciton has bulk-like behavior, can be assumed to be equal to the actual film thickness $d$ ($d_{eff} = d$). The effect of the surface (confining) potential on the exciton translational motion will be taken into account by using appropriate boundary conditions. So, the Hamiltonian for the center-of-mass motion of the ground-state (1$s$) exciton is given by

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla^2 + E_{gap} + E_r. \qquad (2)$$

Here, $E_r$ is the ground-state eigenenergy associated with the relative motion, $M = m_e + m_h$ is the total exciton mass, $m_e(m_h)$ is the electron (hole) effective mass, $E_{gap}$ is the energy gap between the conduction and valence bands.

To analyze exciton center-of-mass states in a surface-disordered thin film, we shall derive the retarded Green's function $G(\boldsymbol{r}, \boldsymbol{r}')$ which obeys the equation

$$[E + i\hbar\nu_0 - \hat{H}]G(\boldsymbol{r}, \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad (3)$$

and satisfies the Dirichlet boundary conditions:

$$G(z = \xi(x)) = 0, \qquad G(z = d) = 0. \qquad (4)$$

In Eq. (3), $E$ denotes the exciton total energy. Besides, we have introduced a homogeneous bulk damping $\nu_0$ to take into account its effect on the scattering of the exciton center-of-mass from the rough surface.

Making use of the Green's theorem, we have derived a Dyson-type integral equation to relate the Green's function $G$, perturbed by surface disorder, with the Green's function $G_0$ for the ideal thin film with $\xi(x) = 0$:

$$G(\boldsymbol{r}, \boldsymbol{r}') = G_0(\boldsymbol{r}, \boldsymbol{r}') + \int_{-\infty}^{\infty} dx_1 G_0(\boldsymbol{r}, \boldsymbol{r}_1)V(\boldsymbol{r}_1)G(\boldsymbol{r}_1, \boldsymbol{r}'). \qquad (5)$$

Here, the kernel $V(\boldsymbol{r}_1)$ has the meaning of the exciton center-of-mass scattering potential and in the first order in $\xi$ is given by

$$V(\boldsymbol{r}_1) \equiv \frac{\overleftarrow{\partial}}{\partial z_1}\bigg|_{z_1=0} \frac{\hbar^2}{2M}\xi(x_1)\frac{\overrightarrow{\partial}}{\partial z_1}\bigg|_{z_1=0}. \qquad (6)$$

The arrows over the derivatives indicate the direction of the operation.

We have also averaged the Eq. (5) for $G$ by employing the technique proposed in [10]. The resulting equation for the average Green's function $\bar{G} \equiv \langle G \rangle$ within the self-consistent Born approximation can be symbolically written as

$$\bar{G} = G_0 + G_0 \langle \hat{V} \bar{G} \hat{V} \rangle \bar{G}. \tag{7}$$

The solution of Eq. (7) can be expressed as

$$\bar{G}(x - x'; z, z') = \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \bar{G}(k_x; z, z') e^{ik_x(x-x')}, \tag{8}$$

where

$$\bar{G}(k_x; z, z') = \frac{G_0(k_x; z, z')}{1 - \kappa k_z \zeta^2 \cot(k_z d)}. \tag{9}$$

Here, $k_z = k_z(k_x) = [2M/\hbar[\omega - \omega_T + i\nu_0] - k_x^2]^{1/2}$, $\omega = E/\hbar$, and $\omega_T = (E_{gap} + E_r)/\hbar$. Because of the self-consistency, the quantity $\kappa$ in Eq. (9) satisfies an integral equation that directly follows from Eq. (7). In the case of normal incidence of light ($k_x = 0$), the equation for $\kappa$ takes the form

$$\kappa = \int_{-\infty}^{\infty} \frac{dk_x'}{2\pi} W(k_x') \Delta_\kappa(k_x') k_z', \tag{10}$$

$$\Delta_\kappa(k_x') = \frac{\cot(k_z' d)}{1 - \kappa k_z' \zeta^2 \cot(k_z' d)}, \tag{11}$$

where $W(k_x)$ is the Fourier transform of the correlator $W(|x|)$. In accordance with the expression (9) for the function $\bar{G}(k_x; z, z')$, the exciton resonances, which in the case of an ideal thin film appear at frequencies satisfying the relation $k_z(\omega_n)d = n\pi$ $(n = 1, 2, \ldots)$, are shifted and broadened by the scattering of the exciton the rough surface. The broadening $\nu$ and shift $\Delta\omega$ of exciton resonances are given by

$$\nu(\omega) = -\frac{\hbar}{M} \zeta^2 k_z^3 \, \mathrm{Im}(\kappa), \tag{12}$$

$$\Delta\omega(\omega) = \frac{\hbar}{M} \zeta^2 k_z^3 \, \mathrm{Re}(\kappa). \tag{13}$$

It should be noted that the form of the frequency dependencies of $\nu$ and $\Delta\omega$ is determined by the relation between the variation scales $1/R_c$ and $\sqrt{2M(\nu + \nu_0)/\hbar}$ of functions $W(k_x)$ (10) and $\Delta_\kappa(k_x)$ (11), respectively.

## 3. Numerical results

Using Eqs. (10)–(13), we have calculated the surface-induced broadening $\nu$ (Fig. 1) and shift $\Delta\omega$ (Fig. 2) in the $Z_3$ exciton region of a CuCl thin film. The

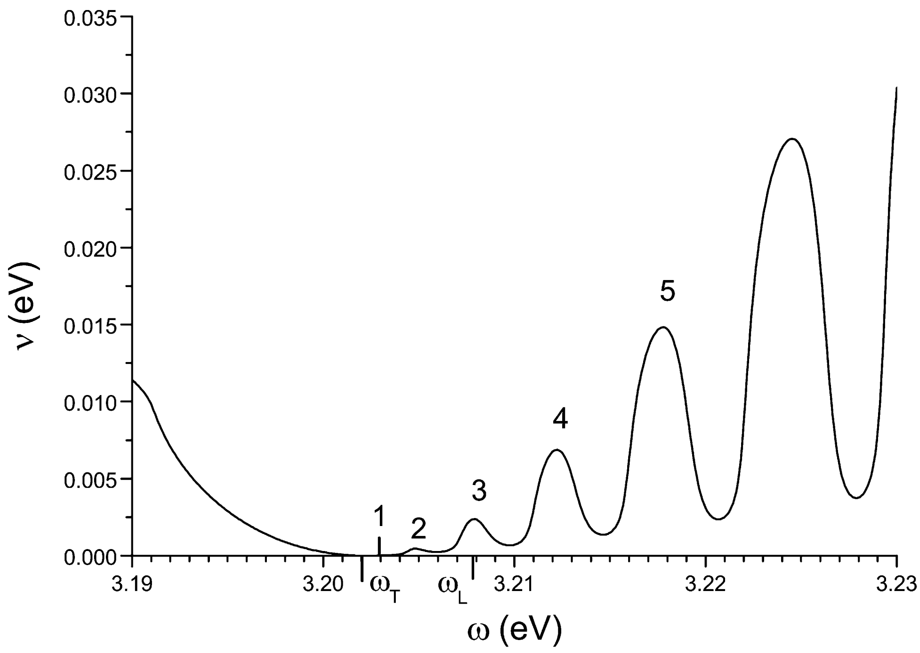


Fig. 1. Surface-induced inhomogeneous broadening $\nu$ of $Z_3$ exciton resonances in a CuCl thin film.

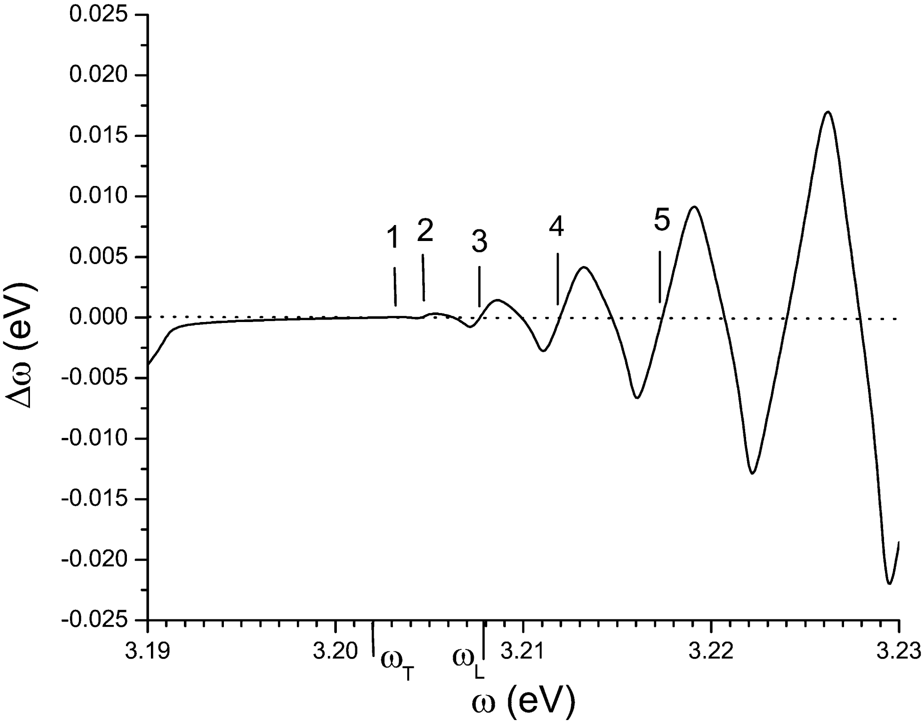


Fig. 2. Surface-induced shift $\Delta\omega$ of $Z_3$ exciton resonances in a CuCl thin film.

parameters used in the calculation are: $d = 165$ Å, $\omega_T = 3.2022$ eV, $v_0 = 0.3$ meV, $\zeta = 6$ Å, $R_c = 100$ Å.

The inhomogeneous broadening $v$ (Fig. 1) exhibits resonances at frequencies close to the eigenvalues $\omega_n = \omega_T + (\hbar/2M)(n\pi/d)^2$ of the quantized exciton in the thin film. The line-shape of each resonance in $v(\omega)$ is practically *symmetric* with respect to its maximum at $\omega \approx \omega_n$ and *broad* since $1/R_c \ll \sqrt{2M(v+v_0)/\hbar}$ with the chosen parameters. We should emphasize that the described behavior of each resonance of $v(\omega)$ is a characteristic prediction of the self-consistent approach, which takes into account the action of $v$ on itself. Indeed, within the usual Born approximation, when Eq. (11) reduces to a similar expression, but with $\kappa = 0$, the *symmetric broad* resonances in $v$ (Fig. 1) would appear only at extremely larger values of the correlation radius $R_c$.

Another interesting feature of $v(\omega)$ is the considerably increase of its average value at $\omega > \omega_T$ (see Fig. 1). Such an increase of $v$ with $\omega$ agrees very well with the phenomenological models for $v(\omega)$ employed in the works [4–6] to explain optical spectra of CuCl thin films. Our results show that exciton-surface scattering contributes considerably to the damping factor for very thin films.

As is seen in Fig. 2, the quantity $\Delta\omega$ vanishes at frequencies $\omega_n$ and, hence, the exciton resonances in the case $1/R_c \ll \sqrt{2M(v+v_0)/\hbar}$ are not shifted. In addition, $\Delta\omega$ is negative on the left side of each exciton resonance and positive on the right side. Therefore, the effect of $\Delta\omega$ on exciton resonances turns out to be analogous to that of broadening.

## 4. Conclusion

We have applied the self-consistent Green's function method to derive and analyze the surface-induced inhomogeneous broadening $v$ and shift $\Delta\omega$ of exciton resonances in the thin film regime. The dependencies of $v$ and $\Delta\omega$ on the parameters of the excitonic film and its disordered interface were found. Also, we analyzed the behavior of $v$ and $\Delta\omega$ in the $Z_3$ exciton region of CuCl thin films. This analysis shows that the inhomogeneous broadening $v$ has resonances at the eigenfrequencies $\omega_n$ of quantized excitons in the thin film. Thanks to the self-consistency, i.e. the action of $v$ on itself, the resonances in $v$ are *symmetric* and *broad* for typical values of the correlation radius $R_c$. Besides, the shift $\Delta\omega$ at the eigenfrequencies $\omega_n$ vanishes.

## Acknowledgements

This work was partially supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT) under Grant no. 36047-E.

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