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Changes in Optical Characteristics of Dielectric Nanofilm Structures in Relation to Bulk Ones

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Abstract − A microscopic theory of optical properties of ideal ultrathin molecular films, was formulated in bosonic and nearest-neighbor approximation. Calculating of dynamical permittivity by the single-pole Green's functions have shown that the threshold of light absorption, refraction, reflection and transmission can be moved along frequencies, changing the film thickness. This can give a great contribution to practical ultrathin film engineering, especially to construction of drug delivery nanoparticles in nanomedicine.

I. Introduction

Theoretical studies of quasi-two-dimensional exciton systems became rather intense, especially in application of device packaging. Electronic (nano)components are used today in extreme physical conditions and in that sense, ultrathin dielectric crystalline films could be used as surface layers for electronic or drug component protection [1–4]. We study the basic physical characteristics of ultrathin molecular crystalline films and one can see that essential properties of these systems arise with perturbational conditions which appear AT and WITHIN their surface layers.

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Theoretical analysis is based on the standard exciton Hamiltonian for low exciton concentrations, in harmonic (Bose) approximation, and nearest-neighbors approximation [5,6] (because orbitals overlap only for neighbor molecules):

$$H = \sum_{\vec{n}} \Delta_{\vec{n}} B^{+}_{\vec{n}} B_{\vec{n}} + \sum_{\vec{n},\vec{\lambda}} X_{\vec{n},\vec{n}+\vec{\lambda}} B^{+}_{\vec{n}} B_{\vec{n}+\vec{\lambda}} \,. \qquad (1)$$

where $\Delta_{\vec{n}}$ denotes the excitation energy of an isolated molecule localized at the site $\vec{n} \equiv (n_x, n_y, n_z)$ while $X_{\vec{n}\vec{m}}$ represent the matrix elements of dipole-dipole interaction, i.e. the energy transfer of exciton from site $\vec{n}$ to site $\vec{m}$. The ultrathin molecular film (thickness: $L = Na$, $N \leq 10$, a − lattice constant) has a simple cubic structure, with two parallel (XY) infinite surfaces [7]. Energy parameters of our model are narrowed in boundary layers as:

$$\begin{aligned} \Delta_{\vec{n}} \;&\rightarrow\; \Delta_{n_z} = \Delta\left(1 + d_0\delta_{0,n_z} + d_N\delta_{N,n_z}\right) ; \\ X_{\vec{n},\vec{n}+\vec{\lambda}} \;&\rightarrow\; X_{n_z,n_z\pm1} \,: \\ & X_{n_z,n_z+1} = -|X|\left(1 + x_0\delta_{0,n_z} + x_N\delta_{N-1,n_z}\right) ; \\ & X_{n_z,n_z-1} = -|X|\left(1 + x_0\delta_{1,n_z} + x_N\delta_{N,n_z}\right) . \end{aligned}$$

The dispersion law for the exciton will be determined by Green's function method [8–10]. The aim is to study single-exciton two-time dependent commutator Green's function $G_{\vec{n}\vec{m}}(t) = \langle\langle B_{\vec{n}}(t) \mid B^{+}_{\vec{m}}(0)\rangle\rangle$ and corresponding equation of motion. Performing the time and partial spatial (XY) Fourier-transformation in the nearest neighbor approximation we obtain the system of $N+1$ nonhomogeneous algebraic-difference equations:

$$\begin{aligned} & \left(1 + x_0\delta_{0,n_z} + x_N\delta_{N-1,n_z}\right) G_{n_z+1,m_z} + \\ + \;& \left[\varrho - \frac{\Delta}{|X|}\left(d_0\delta_{0,n_z} + d_N\delta_{N,n_z}\right)\right] G_{n_z m_z} + \\ + \;& \left(1 + x_0\delta_{1,n_z} + x_N\delta_{N,n_z}\right) G_{n_z-1,m_z} = \mathcal{K}_{n_z m_z} \,, \end{aligned} \qquad (2)$$

where: $\mathcal{K}_{n_z m_z} \equiv \dfrac{i\hbar}{2\pi|X|}\delta_{n_z m_z}$ and

$$\varrho = \frac{\hbar\omega - \Delta}{|X|} + 2\left(\cos ak_x + \cos ak_y\right) . \qquad (3)$$

The determination of Green's function poles, which define the spectrum of possible exciton energies, reduces to the calculation of the roots of the determinant of the system of equations:

$$\begin{aligned}\mathcal{D}_{N+1}(\varrho) &= \left(\varrho - \frac{\Delta}{|X|}d_0\right)\left(\varrho - \frac{\Delta}{|X|}d_N\right)\mathcal{C}_{N-1} - \\ &- \left[\left(\varrho - \frac{\Delta}{|X|}d_0\right)(1+x_N)^2 + \right. \qquad (4)\\ &+ \left.\left(\varrho - \frac{\Delta}{|X|}d_N\right)(1+x_0)^2\right]\mathcal{C}_{N-2} + \\ &+ (1+x_0)^2(1+x_N)^2\mathcal{C}_{N-3}\,,\end{aligned}$$

where C_N are the characteristic N-th order Tchebychev's polynomials ($C_{N-1} = \varrho C_N - C_{N+1}$).

In general, the equation $\mathcal{D}_{N+1}(\varrho) \equiv 0$ is not analytically solvable so numerical methods must be applied. For given numerical values of 5 boundary parameters N (we put $N = 4$), $d_{0/N} \in (-0,2; +0,2)$ and $x_{0/N} \in (-0,5; +1,0)$, from the equation (4) one can obtain the numerical values for ϱ_ν; $\nu = 1, 2, 3, \ldots, N+1$.

Diagonal Green's functions (determining equilibrium properties) of thin films are multi-pole (denominator is a polynomial function of $(N+1)$-th order) so we must factorize them to single pole terms:

$$G_{n_z n_z} = \frac{i\hbar}{2\pi|X|}\sum_{\nu=1}^{N+1}\frac{g_{n_z}(\rho_\nu)}{\varrho - \rho_\nu}\,, \qquad (5)$$

where spectral weights are [10]:

$$g_{n_z}(\varrho_\nu) = \frac{D_{n_z n_z}(\varrho_\nu)}{\left.\dfrac{d}{d\varrho}D_{N+1}(\varrho)\right|_{\varrho=\rho_\nu}}\,. \qquad (6)$$

One can see that the spectral weights determine space distribution of excitons, i.e. probability to find particular exciton on the particular layer of ultrathin film, with particular (discrete) energy.

III. Permittivity and absorption index

The expression for the relative permittivity of the system has the following form [11−13]:

$$\mathcal{E}_r^{-1}(\omega) = 1 - 2\pi i S\left[G(+\omega) + G(-\omega)\right]\,, \qquad (7)$$

where: $S = \dfrac{\tau_0 E_0^2}{8\pi\hbar}$ (τ_0 is the elementary cell volume and E_0 is the electrical field per elementary cell). We can rewrite this expression using the factorized multi-pole Green's functions (7) of perturbed film:

$$\mathcal{E}_{n_z}^{-1} = 1 - \frac{\hbar S}{|X|}\sum_{\nu=1}^{N+1}\sum_{s=+,-}\frac{g_{n_z}(\varrho_\nu)}{\varrho_s - \varrho_\nu}\,, \qquad (8)$$

where: $\varrho_\pm = \dfrac{\mp\hbar\omega - \Delta}{|X|} + 2(\cos a_x k_x + \cos a_y k_y)$, and denoting $\dfrac{\Delta}{|X|} \equiv |p|$ and recalculating this expression one can get:

$$\mathcal{E}_{n_z}^{-1}(\omega) = 1 - \frac{2\hbar S}{|X|}\sum_{\nu=1}^{N+1} g_{n_z}(\varrho_\nu)\times \qquad (9)$$

$$\times\frac{\varrho_\nu - |p| - 2(\cos a_x k_x + \cos a_y k_y)}{\left(\dfrac{\hbar\omega}{|X|}\right)^2 - \left[\varrho_\nu - |p| - 2(\cos a_x k_x + \cos a_y k_y)\right]^2}\,.$$

Our scope of research are optic, i.e. absorption properties of the observed model example. The refraction (n) and absorption (κ) indices are usually defined in the literature [5,10] by permittivity term: $\sqrt{\mathcal{E}} = n + i\kappa$. Introducing the complex frequency: $\omega \to \omega + i\upsilon$ in expression for permittivity (9), we get complex permittivity: $\mathcal{E} = \mathcal{E}' + i\mathcal{E}$", where: $\mathcal{E}' \equiv \mathcal{E}'_{n_z}(\omega) = \mathrm{Re}\{\mathcal{E}\}$ and $\mathcal{E}" \equiv \mathcal{E}"_{n_z}(\omega) = \mathrm{Im}\{\mathcal{E}\}$. Based on this, we can find the expression for absorption and refraction indices in the following form:

$$\begin{aligned}\kappa_{n_z}(\omega) &= \sqrt{\frac{\mathcal{E}'}{2}\left[\sqrt{1 + \left(\frac{\mathcal{E}"}{\mathcal{E}'}\right)^2} - 1\right]}\,;\\ n_{n_z}(\omega) &= \sqrt{\frac{\mathcal{E}'}{2}\left[\sqrt{1 + \left(\frac{\mathcal{E}"}{\mathcal{E}'}\right)^2} + 1\right]}\,.\end{aligned} \qquad (10)$$

The reflection (r) and transparency (t) indices are defined [5,10] by the refraction and absorption ones:

$$\begin{aligned}r_{n_z}(\omega) &= \frac{\left[n_{n_z}(\omega) - 1\right]^2 + \kappa_{n_z}^2(\omega)}{\left[n_{n_z}(\omega) + 1\right]^2 + \kappa_{n_z}^2(\omega)}\,;\\ t_{n_z}(\omega) &= 1 - n_{n_z}(\omega) - \kappa_{n_z}(\omega)\,.\end{aligned} \qquad (11)$$

From this and expressions (9) – (11) one can see that all optical characteristics of the film depends

on position of film-layer. In difference with research performed so far [11-15] here we want to define optical properties of whole film in the direction perpendicular to film. Those (additive) quantities are gain simply by summing of all values of adequate quantities by film layers, i.e.

$$\mathcal{OC}(\omega) = \sum_{n_z=0}^{N} \mathcal{OC}_{n_z}(\omega)\,, \tag{12}$$

where $\mathcal{OC} \equiv \{\kappa,\, n,\, r,\, t\}$.

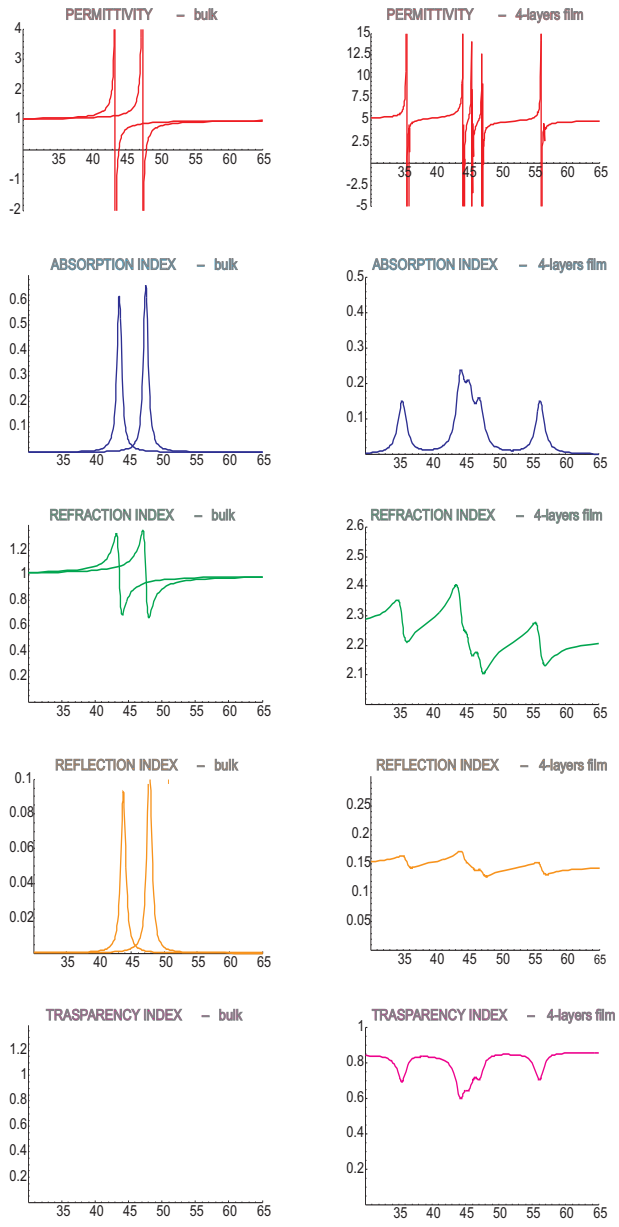

Figure 1: Optical characteristics of ultrathin film

Graphs on Fig. 1 show dependence of relative dynamic permittivity, absorption, refraction, reflection and transparency indices on the energy or frequency of external electro-magnetic field ($\widetilde{\omega} \equiv \hbar\omega/|X|$), for a center of Brilouin's zone, and in two cases:

a) for molecular bulk-structures – left column,

b) for four-layered ideal[1] molecular film-structures – right column.

One can see from presented graphics, that the film-structures have discrete and selective optical properties compared to bulk ones. There are 5 discrete absorption lines, equal to number of possible (macro) quantum states of excitons through film-thickness.

Instead of one zone of relative permittivity for bulk (on the top graphic from left only borders of that zone are denoted), in the case of films there are 5 separated resonant lines, from which 2 are very distant from bulk-borders.

For the case of bulk there is completely clear absorption zone (on the second graphic from left only borders of that zone are denoted), while for the case of films there are 5 absorption peaks corresponding to the resonant lines.

Refraction indices have jumps on the places where absorption index changes: for the bulk that is happening on the borders of absorption zone, while film has 5 corresponding, not very narrow peaks.

Reflection for the bulk is only at the borders of absorption zone, for films reflection is happening partially at each crystallographic plane of film.

The most interesting result is definitely non-transparency of molecular bulk crystal (lower figure from left), but when it's thinned to the film of nano-size it's becoming transparent except for 5 discrete peaks which are corresponding to combination of absorption and reflection peaks of film.

Consequently with space symmetry, we get symmetrical situation for peaks distribution.

[1]Ideal film denotes model of sample with two very close parallel border surfaces along one spatial direction [11-15], while in the other two is infinite. Film thickness is only several nanometers (in this case: 4 constants of lattice), while on borders there are no perturbations of fundamental physical parameters. Film has same crystallographic structure as the bulk.

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IV. Conclusion

Results of this analysis confirm the essential differences in dispersion law of excitons in film structures in comparison with unbounded ones, which is an exclusive consequence of boundaries existence. Consequences of this fact are different optical properties of film-structures.

Characteristic resonant peaks appear in the dependence of absorption index of ultrathin film on frequency of external electro-magnetic field. All peaks are in infrared region and respond to absorption of corresponding external electromagnetic frequencies. It means that discrete and selective absorption appears. In accordance to space symmetry of ultrathin film structure, we get symmetrical distribution of absorption peaks.

Contrary to molecular balk-crystal samples which are almost complete absorbers in IR area, ultrathin film-structures are practically completely transparent - except for 5 absorption peaks.

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