

Absorption Features of Symmetric Molecular Nanofilms

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Electronic components are used today in extreme physical conditions and in that sense, ultrathin dielectric crystalline films could be used as surface layers for electronic component protection. Calculating dynamical permittivity by the single-pole Green's functions it was shown that the threshold of light absorption can be moved along frequencies, changing the film thickness and the intensity of boundary perturbations. We study the basic micro and macroscopic physical characteristics of symmetric ultrathin molecular crystalline films and one can see that essential optical properties of these systems arise with perturbation conditions, which appear at their surface layers. Depending on the values of the parameters of surface interactions, certain energy levels can lie outside the energy band of the ideal crystal, so there appear the surface localized states of excitons. Characteristic resonant peaks appear in the dependence of dielectric permittivity and absorption index (extinction coefficient) of ultrathin film on frequency of external electro-magnetic field.

Keywords:

1. INTRODUCTION

Theoretic research of low-dimension crystalline systems (nanostructures: ultrathin films, quantum wires, dots, etc.) have been very much intensified in order to obtain fundamental information about extremely different physical and chemical properties of matter and also because of their wide practical (technical and technological) application in nano-, opto- and bioelectronics.¹ The peculiarity of these “tiny” structures is manifested in that the presence of close boundary surfaces leads to a considerable change of generally known properties of these materials as well as to the occurrence of non-specific phenomena (as a consequence of the effect of dimension quantization²) compared to the characteristics of appropriate ‘bulk’ samples.³

An interest in studying exciton sub-system arose from the very fact that it is the excitons themselves that are responsible for dielectric, optical (absorption, light dispersion, luminescence), photoelectrical and other properties

of crystal.⁴ In this paper we observed ultra-thin dielectric films (the thickness of which does not exceed a dozen atomic planes). Typical representatives of such structures include molecular crystals, in which, in the result of the interaction of the outer electromagnetic field and electrons of crystal, elementary excitations arise—excitons. Relative permittivity is theoretically defined by way of exciton dispersion laws and their density state, and in turn, optical properties of the observed system are defined through relative permittivity.

2. EXCITON MODEL OF NANOFILM STRUCTURE

The standard expression for effective Hamiltonian in harmonic approximation⁴ has the following form:

$$H = \sum_{\vec{n}} \Delta_{\vec{n}} B_{\vec{n}}^{\dagger} B_{\vec{n}} + \sum_{\vec{n}, \vec{m}} X_{\vec{n}\vec{m}} B_{\vec{n}}^{\dagger} B_{\vec{m}} \quad (1)$$

whereby $B_{\vec{n}}^{\dagger}$ and $B_{\vec{n}}$ are creation and annihilation exciton operators on node \vec{n} of crystalline lattice, $\Delta_{\vec{n}}$ represents

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the energy of isolated exciton on that node, while $X_{\vec{n}\vec{m}}$ are matrix elements of exciton transfer from node \vec{n} to node \vec{m} . The model assumes that the energy of excitons on node is by $\sim 10^2$ bigger than the energy of its transfer.

The systems limited by two parallel surfaces are referred to as films.^{5,6} Dimensions of crystalline nano-film are such it is unlimited in XY , while in z -direction it has a finite—very small thickness $L = Na$, whereby: $N < 10$ —number of parallel crystallographic planes (including 2 border planes), and a is a constant of crystal lattice.

We will observe symmetrical dielectric nano-film (Fig. 1), which can be practically made by controlled reaching of bulk samples.⁶ Due to the existence of border areas of exciton energy on nodes, energy transfers between border ($n_z = 0$; $n_z = N$) and their adjacent planes ($n_z = 1$; $n_z = N - 1$) are perturbed, which can be presented in the following manner:^{6,7}

$$\begin{aligned}\Delta_{\vec{n}} &\equiv \Delta[1 + d(\delta_{n_z,0} + \delta_{n_z,N})] \\ X_{\vec{n},\vec{n}+\vec{\lambda}} &\equiv X[1 + x(\delta_{n_z,0} + \delta_{n_z,N-1})] \\ X_{\vec{n},\vec{n}-\vec{\lambda}} &\equiv X[1 + x(\delta_{n_z,1} + \delta_{n_z,N})]\end{aligned}\quad (2)$$

whereby parameter d defines perturbation on node of border areas and parameter x defined perturbation of transfer in border layers along the z -direction.

We will carry out micro-theoretical analysis of exciton sub-system in ultrathin crystalline molecular films by using the method of Green functions. We will observe the following Green function:⁸ $G_{\vec{n}\vec{m}}(t) = \langle\langle B_{\vec{n}}(t) | B_{\vec{m}}^+(0) \rangle\rangle$, which satisfies the following movement equation:

$$i\hbar \frac{d}{dt} G_{\vec{n}\vec{m}}(t) = i\hbar \delta(t) \delta_{\vec{n}\vec{m}} + \Delta_{\vec{n}} G_{\vec{n}\vec{m}}(t) + \sum_{\vec{l}} X_{\vec{n}\vec{l}} G_{\vec{l}\vec{m}}(t) \quad (3)$$

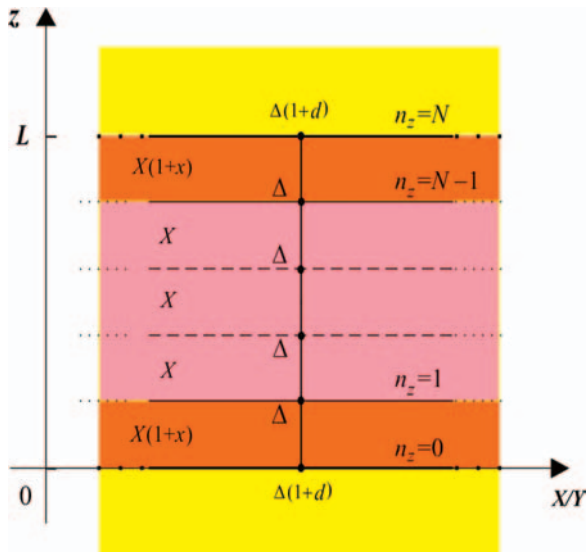


Fig. 1. Model of symmetrical ultrathin dielectric film.

After full time- and now only partially spatial Fourier transform of these equations, the following is arrived at:

$$\begin{aligned}G_{n_z, m_z} &\left[\rho - \frac{\Delta}{|X|} d(\delta_{n_z,0} + \delta_{n_z,N}) \right] \\ &+ G_{n_z+1, m_z} [1 + x(\delta_{n_z,0} + \delta_{n_z,N-1})] \\ &+ G_{n_z+1, m_z} [1 + x(\delta_{n_z,1} + \delta_{n_z,N})] = \frac{i\hbar}{2\pi|X|} \delta_{n_z, m_z}\end{aligned}\quad (4)$$

with the introduction of the designation: $\rho = (\hbar\omega - \Delta) \cdot |X| + 2(\cos ak_x + \cos ak_y)$.

Equation (4) represents a system of $N + 1$ non-homogenous algebra-differential equations for Green functions. As in order to find the dispersion laws we need only the poles of these functions, it is sufficient to find the system determinant and equalize it with zero. In this way we obtain $N + 1$ solution $\rho \equiv \rho_\nu$; $\nu = 1, 2, \dots, N + 1$.

3. NANOFILM PERMITTIVITY

Spectral weights of specific Green functions should be calculated in order to find the probability of occurrence and spatial distribution of exciton conditions in a film. We start from the system of equations for Green functions (4), but written in matrix form:

$$\hat{D}_{N+1} \tilde{G}_{N+1} = \hat{K}_{N+1}, \quad (5)$$

whereby \hat{D}_{N+1} is a matrix that corresponds to the system determinant, while \tilde{G}_{N+1} and \hat{K}_{N+1} are vectors of Green functions and Kronecker deltas, respectively. If in (5) we act with inverse matrix \hat{D}_{N+1}^{-1} from the left and keeping in mind that the inverse matrix may be expressed by way of adjunct matrix, the members of which D_{ik} are co-factors of element d_{ik} of direct matrix, by further calculus/calculation we can arrive at/obtain Green functions, in the numerators of which spectral weights $g_{n_z}(\rho_\nu)$ directly figure, that is to say, the probability of finding exciton conditions ρ_ν .^{7,8}

$$G_{n_z} = -\frac{i\hbar}{2\pi|X|} \sum_{\nu=1}^{N+1} \frac{g_{n_z}(\rho_\nu)}{\rho - \rho_\nu} \quad (6)$$

When determining the dynamic permittivity of film we shall use a general expression,^{6,9} only by taking strict account that Green functions, and even permittivity, depend on (the number, i.e., position) of crystallographic planes of symmetrical film n_z :

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - 2\pi i F [G_{n_z}(\omega) + G_{n_z}(-\omega)] \quad (7)$$

whereby F -is structural factor.^{4,5} By incorporating the expression for Green functions (6) the following is obtained:

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - \frac{\hbar F}{|X|} \sum_{\nu=1}^{N+1} \sum_{s=+, -} \frac{g_{n_z}^s}{\rho_s - \rho_\nu} \quad (8)$$

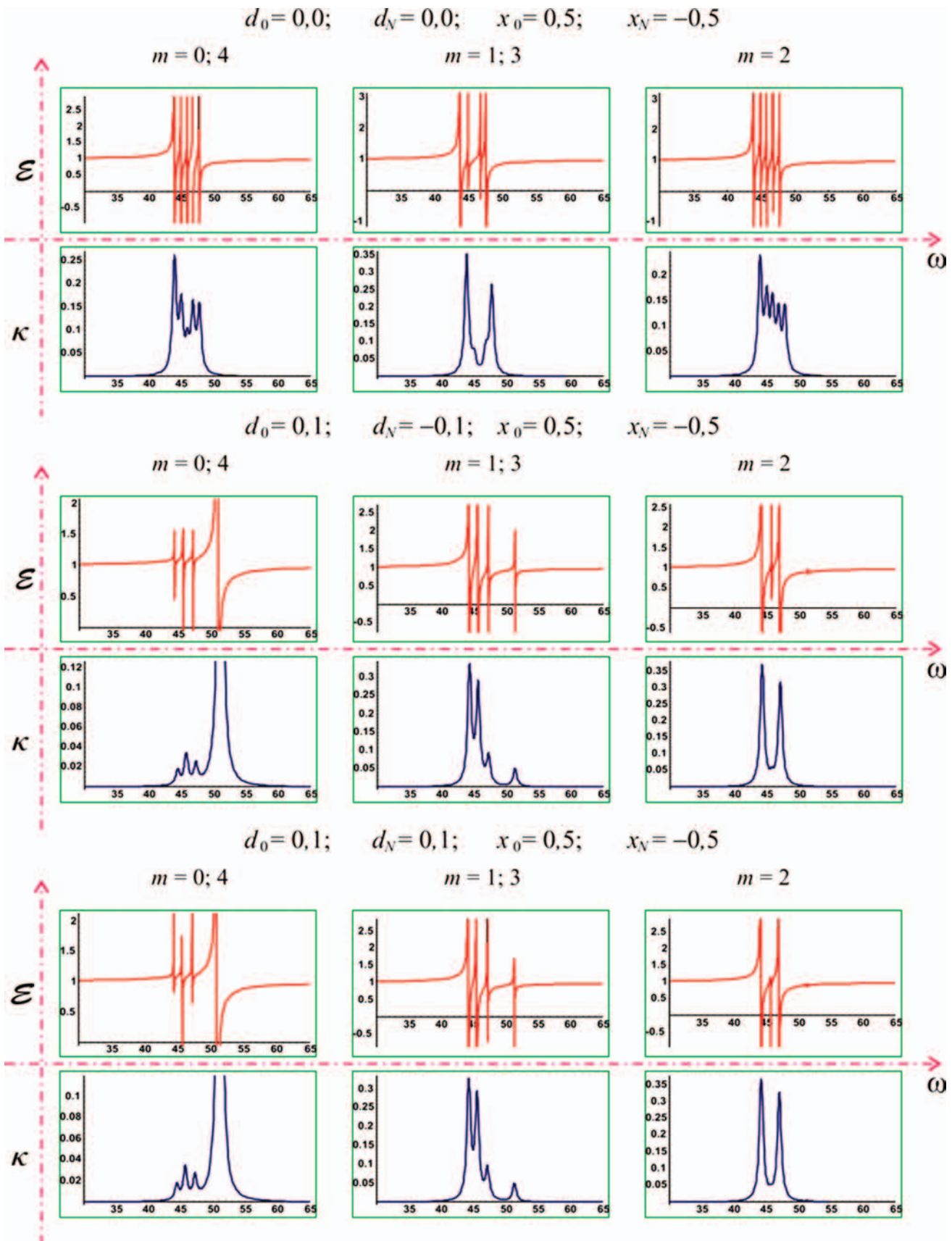


Fig. 2. Relative permittivity and absorption index of symmetrically perturbed four-layer film depending on reduced frequency.

whereby: $\rho_{\pm} = (\mp \hbar \omega - \Delta)/|X| + 2(\cos ak_x + \cos ak_y)$, and with a little analytical arrangement, the expression (8) is transformed to:

$$\varepsilon_{n_z}(\omega) = \left\{ 1 - \frac{2\hbar F}{|X|} \sum_{\nu=1}^{N+1} g_{n_z}^{\nu} \times \frac{\rho_{\nu} - \Delta/|X| - 2(\cos ak_x + \cos ak_y)}{(\hbar \omega/|X|)^2 - [\rho_{\nu} - \Delta/|X| - 2(\cos ak_x + \cos ak_y)]^2} \right\}^{-1} \quad (9)$$

This expression represents dependence of relative dynamic permittivity upon the frequency of initial electromagnetic excitation, i.e., a dielectric response of observed symmetrical molecular film to the outer electromagnetic field.

4. ABSORPTION IN NANOFILM

Dielectric permeability, i.e., permittivity in case of existence of dispersion is complex parameter (frequency dispersion of dielectric permeability $\varepsilon(\omega)$ implies its dependence on frequency ω), i.e., it can be expressed by way of real and imaginary part: $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$. By way of simple relations ε' and ε'' they are connected with optical characteristics of the ambience: refraction index and absorption ratio (Kramers-Kronig's relation).

Maxwell already demonstrated that the dielectric constant of the ambience is equal to the square of refraction index: $\varepsilon(\omega) \equiv \eta^2(\omega)$. If complex refraction index is introduced: $\eta = n + i\kappa$, it is easy to arrive at the expression for dynamic index of absorption (or extinction coefficient) in the following form:

$$\kappa_{n_z}(\omega) = \sqrt{\frac{\varepsilon'_{n_z}(\omega)}{2} \left\{ \sqrt{1 + \left[\frac{\varepsilon''_{n_z}(\omega)}{\varepsilon'_{n_z}(\omega)} \right]^2} - 1 \right\}} \quad (10)$$

Figure 2 represent dependencies of relative dynamic permittivity and absorption index on reduced energy of outer electromagnetic radiation for symmetrically perturbed four-layer film. In all figures these dependencies are shown for outer (border) surfaces (left graphs with: $m = 0$ and 4), first internal surfaces (graphs in the middle with: $m = 1$ and 3) and central crystallographic surface (right graphs with: $m = 2$). The occurrence of resonant peaks is visible, the count and distribution of which very much depends on the value of border perturbation parameters.

The first upper figure that contains 3 graphs shows permittivity, and the other three—absorption index of more weakly perturbed ultrathin symmetrical film (when perturbation parameters assume the following values: $d = 0$, 1 and $x = 1$, 0) with 4 inter-atomic layers, i.e., two border and three more internal crystallographic planes parallel to border planes. The penultimate figure with 3 graphs shows permittivity, and the last—absorption index of the

same film strongly perturbed (when perturbation parameters assume the following values: $d = 0$, 2 and $x = 2$, 0). A more detailed analysis of the influence of perturbation parameters was presented in, e.g., Refs. [10–12]. We shall here pay attention to the analysis of absorption characteristics of observed film-structure. All the presented graphs show that the number of resonant peaks depends on the number, i.e., position of atomic plane n_z (i.e., on number m) for which the absorption index is calculated. Likewise, it is visible that the number of absorption peaks (number of “real” “peaks”) is not equal to the number of resonant peaks of relative permittivity (when $\varepsilon(\omega_r) \rightarrow \pm\infty$), but is smaller than it. This means that the absorption is more discrete and that there are priority frequencies of outer electromagnetic radiation that are fully absorbed. With others, absorption is only partial. It is shown that on border surfaces of this film practically only one—very narrow absorption area can appear.

The influence that the perturbation parameters have is not as significant as the influence of very small thickness of film: increase of value of parameter d moves the center of absorption toward somewhat higher frequencies, while an increase in value of parameter x slightly widens the absorption interval or reduces resonant lines, at the same time “strengthening” one of two possible 5 peaks.

Together with the previous results,¹² we presented here possible absorption with ultrathin—four-layer film, however this is already enough to be able to conclude that the next investigation of the influence of perturbation parameters with extremely thin—two-layer film-structure will show considerably stricter discreteness and selectivity of absorption characteristics of film layers.

5. CONCLUSION

The results of these analyses showed significant differences in dielectric response (macroscopic, as well as dimensional-quantum and conformation properties) of excitons between bulk and film-structures as an exclusive consequence of limitation of film along the z -direction and the existence of perturbation of parameters on border surfaces and border layers of the structure.

Instead of continual absorption zone, mainly in IC area with molecular bulk-structures, absorption peaks appear with films at certain—very narrow frequency intervals of outer electromagnetic field. They show the property of selectiveness, i.e., occurrence of almost completely discrete (resonant) absorption peaks at exactly determined energies, the count and the distribution of which depend on the number of layers in the film and on the value of perturbation parameters.

These properties give the films the advantage compared to bulk structures (the dielectric response of which is continuous within a certain energy band), because in that case films may be used as filters for outer radiation.

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