

# Successive absorption and refraction in ultrathin molecular nano-films

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**Abstract**—Based on the formed model of nano-film crystal structures, changes of optical properties due to the presence of borders for the case of symmetrical ultrathin films are theoretically investigated in this paper. Influence of five border parameters on the occurrence of localized exciton states is examined, as well as their relation with the effects of discretization and selection of resonant absorption of present electromagnetic radiation. Used combined analytical-numerical calculation to find the allowed energy states of excitons and their spatial distribution (per layers) along the axis perpendicular to surface planes. We determined permittivity for the observed models of these ultrathin dielectric films and explored the influence of boundary parameters on the occurrence of discrete and selective absorption.

**Keywords** - nano-films, excitons, permittivity, absorption.

## I. INTRODUCTION

\*Obtaining fundamental information on different physical and chemical properties of materials and their wide practical (technical and technological) applications in nano-, bio- and optoelectronics intensified the theoretical research of low dimensional crystal system (nanostructures: ultrathin films, quantum wires and quantum dots and so on. [1]). Compared with characteristics of appropriate "big" samples, specificity of these "small" structures is reflected in the fact that the presence of close boundary surfaces leads to altered very general known properties of these materials and the occurrence of non-specific phenomenon (as a result of the effects of dimensional quantization) [2,3]. The excitons are responsible for the dielectric, optical (absorption, dispersion of light,

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luminescence), photoelectric and other properties of crystals [4]. In this study we observed ultrathin dielectric films (with a thickness not exceeding of ten atomic planes). Representative examples of these structures are molecular crystals, with in them occurring elementary excitations – excitons, as a result of interaction of the external electromagnetic field and electrons in crystals. Using dispersion law for the excitons and their density of states, we will theoretically define the relative permittivity, and throughout the optical properties of a system.

## II. EXCITONS IN NANO-FILMS

Standard effective excitonic Hamiltonian in harmonic approximation [4,5] has following form:

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

where  $B_{\vec{n}}^{\dagger}$  and  $B_{\vec{n}}$  are operators of creation and annihilation of exciton on site  $\vec{n}$  of crystal lattice;  $\Delta_{\vec{n}}$  represents energy of exciton isolated on this site, and  $X_{\vec{n}\vec{m}}$  are matrix elements of excitons transfer from site to site. In this model we assume that energy of exciton isolated on site is about 100 times bigger compared with the energy needed for transfer of excitons.

We will analyze this system with the method of two-times temperature-dependent Green's functions [6-8] mainly for advantages which this method provides. Green's function has given in following form:

$$G_{\vec{n}\vec{m}}(t) = \langle\langle B_{\vec{n}}(t) B_{\vec{m}}^{\dagger}(0) \rangle\rangle, \quad (2)$$

and satisfied following equation of motion:

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

Systems which have structures containing boundary planes are usually called film-structures [9-11]. Dimensions in crystal nano-films are unlimited in XY directions, while in Z direction has finite width:  $L=Na$ . We will observe dielectric nano-film (Fig.1) which could be made by the controlled doping within bulk structures, or various methods of deposition on substrate materials [11]. Existing boundary layers change energies of excitons on site and transfer of exciton energies between boundary planes ( $n_z=0$  ;  $n_z=N$ ) and first inner planes ( $n_z=1$  ;  $n_z=N-1$ ) within ultrathin film as well, which define perturbation conditions [11-15]:

$$\begin{aligned} \Delta_{\bar{n}} &\equiv \Delta [1+d(\delta_{n_z,0} + \delta_{n_z,N})]; \\ X_{\bar{n},\bar{n}+\bar{\lambda}} &\equiv X [1+x(\delta_{n_z,0} + \delta_{n_z,N-1})]; \\ X_{\bar{n},\bar{n}-\bar{\lambda}} &\equiv X [1+x(\delta_{n_z,1} + \delta_{n_z,N})], \end{aligned} \quad (3)$$

where parameter  $d$  defines perturbation on site of crystal nodes, and parameter  $x$  defines perturbation of energy transfer along Z – axis.

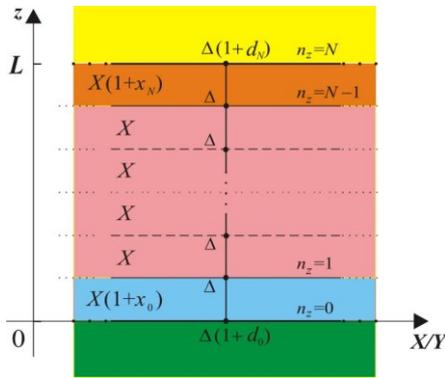


Figure 1. Model of ultrathin film.

Taking into account boundary conditions (3), Hamiltonian (1) and equation of motion (2) we could write equations for the Green's functions [11-15]. After performing of Furrier transformations, unlimited in time but limited in space (limitation is in Z – axe), we get system:

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

where:

$$\rho = \frac{\hbar\omega - \Delta}{|X|} + 2(\cos ak_x + \cos ak_y).$$

System of equations (4) represent system of N+1 non-homogeneous algebraic difference equations for unknown

Green's functions. We actually don't need to find out solution of the system (4), it is sufficient to calculate determinant of system (4) and equalize determinant with zero [11-15], i.e. to calculate poles of the Green's function which define dispersion law of excitons. In such a way we get N+1 solutions  $\rho \equiv \rho_\nu$ ;  $\nu = 1, 2, \dots, N+1$ .

We will present dispersion law for excitons in ultrathin film in non-dimensional form, i.e. calculated reduced energies

$$E_\nu = \frac{\hbar\omega - \Delta}{|X|} \equiv \rho_\nu - R_{xy} \quad (5)$$

in dependence on function  $R_{xy} \equiv 2(\cos ak_x + \cos ak_y)$ . On figures 2 – 4 have shown excitons dispersion laws – on figure 2 for the unperturbed (ideal) film; on figures 3 and 4 for  $d$ -perturbed and  $x$ -perturbed 5-layer film, respectively.

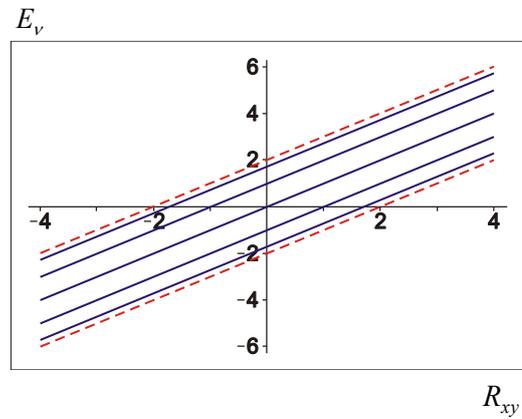


Figure 2. Exciton dispersion law for ideal film.

Comparing nonsymmetrical perturbed (lateral graphics) with symmetrical perturbed (central graphics) films from the figures 3 and 4, one can see clearly nonsymmetrical /symmetrical disposition of the localized states, taking into account that some localized levels overlap in the case of symmetrical perturbation. This overlapping happened only for the  $d$  – perturbation, which is the significant one!

In all graph the full lines represent exciton energy levels in films, while dashed lines represent exciton energy levels in bulk crystals. On the first sight one can see absence of zero energies and the presence of discrete energy levels in film structures. Number of the possible energy states is equal to the number of crystallographic planes within the film along Z-axis.

From the figure 3 one can see that increasing of  $d$  parameter, energy spectra spread on such a way that one energy level move to the higher energies and come out of the bulk energy border. Those energy states are known as localized or Tamm states [4]. Analyzing graphics on the figure 4 one can see that increasing of  $x$  parameter wide the whole spectra with two energy levels which comes out of the bulk energy borders, i.e. with Tamm states.

$E_v$

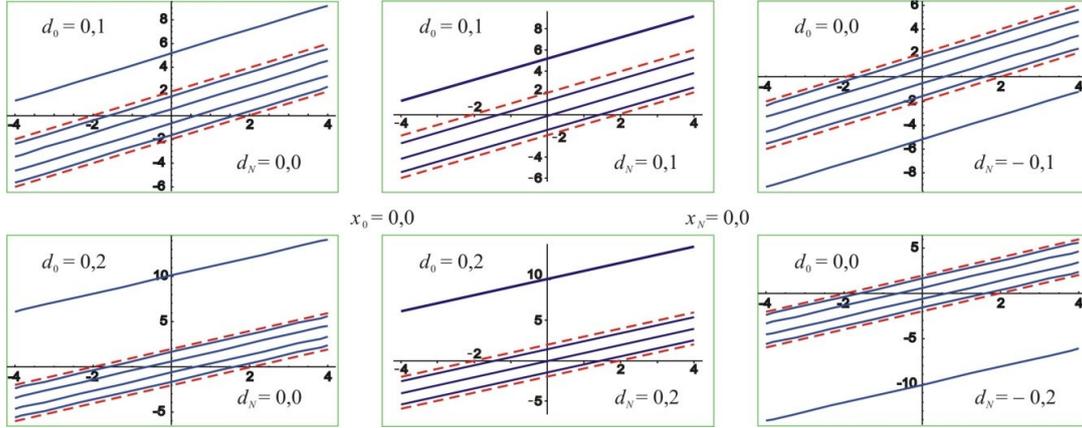


Figure 3. Exciton dispersion law for  $d$ -perturbed 5-layered film.

$R_{xy}$

$E_v$

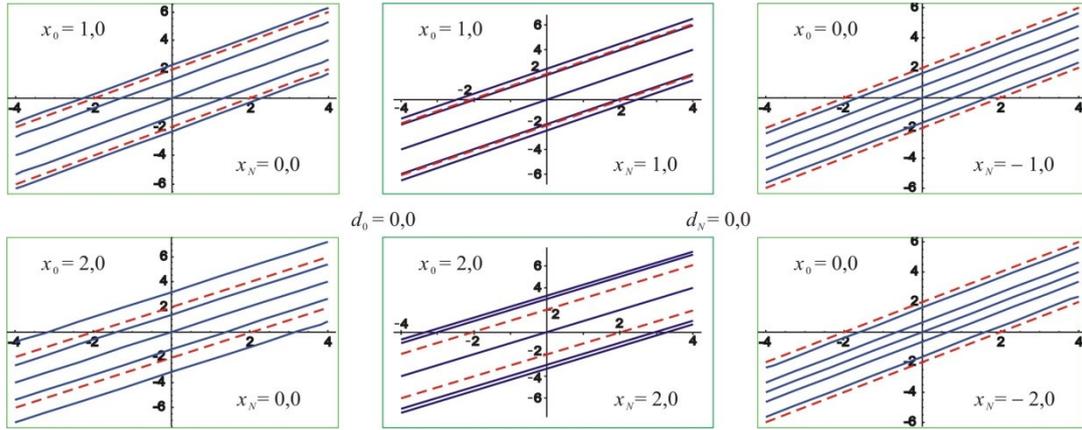


Figure 4. Exciton dispersion law for  $x$ -perturbed 5-layered film.

$R_{xy}$

### III. OCCUPANCY OF EXCITON ENERGY LEVELS AND DIELECTRIC PROPERTIES OF FILMS

To calculate the probability of finding (or creation) of excitons on site and spatial distribution of exciton energy levels within film structures, we need to find out the spectral weight of specific Green's functions. We start from the system of equations for the Green's functions (8), but in matrix form:

$$\hat{D}_{N+1} \tilde{G}_{N+1} = \hat{K}_{N+1}, \quad (6)$$

where  $\hat{D}_{N+1}$  is matrix which represents determinant of the system,  $\tilde{G}_{N+1}$  and  $\hat{K}_{N+1}$  are vectors of Green's functions and Kronecker delta function, respectively. If we imply in (6)

inverse matrix  $\hat{D}_{N+1}^{-1}$  from the left side, knowing that inverse matrix could be represent throughout adjugate (or adjunct) matrix whose terms  $D_{ik}$  are cofactors of elements  $d_{ik}$  of direct matrix, we could calculate Green's functions where numerator represents spectral weight  $g_{n_z}(\rho_v)$ , i.e. probability of finding excitons states  $\rho_v$  [9,11-15]:

$$G_{n_z} = -\frac{i\hbar}{2\pi|X|} \sum_{v=1}^{N+1} \frac{g_{n_z}(\rho_v)}{\rho - \rho_v}. \quad (7)$$

To calculate dynamical permittivity of film we use general expression [4-8], keeping in mind that Green's function (and related dielectric permittivity) are strongly depended of the

number (or site) of the crystalline planes of the symmetrical film:

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - 2\pi i F [G_{n_z}(\omega) + G_{n_z}(-\omega)], \quad (8)$$

where  $F$  is structural factor [4,5]. Including expression for the Green's functions in (8) we obtain:

$$\varepsilon_{n_z}^{-1}(\omega) = 1 - \frac{\hbar F}{|X|} \sum_{v=1}^{N+1} \sum_{s=+,-} \frac{g_{n_z}^v}{\rho_s - \rho_v}, \quad (9)$$

$$\text{where } \rho_{\pm} = \frac{\mp \hbar \omega - \Delta}{|X|} + 2(\cos ak_x + \cos ak_y).$$

Expression (9) shows how dielectric permittivity of ultrathin films depend on frequency (or energy) of external (or initial) electromagnetic excitation. This is actually dielectric response of the symmetrical molecular film on external electromagnetic field.

#### IV. OPTICAL PROPERTIES OF THE FILM

Dispersion of dielectric permittivity (or permeability) is function of their dependence on frequency  $\varepsilon(\omega)$ . With respect to the fact that  $f(t)$  is real function, from the expression:

$$\varepsilon(\omega) = 1 + f(\omega) = 1 + \int_0^{\infty} f(t) e^{-\omega t} dt \quad (10)$$

arise that dielectric permittivity must be complex function, i.e.:

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \quad (11)$$

where  $\varepsilon'$  is their real and  $\varepsilon''$  imaginary part.

Changing the sign of  $\omega$  we obtain that  $\varepsilon(\omega)$  turns into  $\varepsilon^*(\omega)$ , i.e.  $\varepsilon'(-\omega) + i\varepsilon''(-\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ , from where we obtain  $\varepsilon'(-\omega) = \varepsilon'(\omega)$  and  $\varepsilon''(-\omega) = -\varepsilon''(\omega)$ .

Dispersion relation gives opportunity to calculate one of the parts of dielectric permittivity (real or imaginary, which is for example known from the experiment) if we know the other part (imaginary or real), for the whole frequency range. Of course, knowing experimentally data for the whole frequency range is practically impossible, but also not even necessary. For example, if we are interested in  $\varepsilon'(\omega)$  for the frequency  $\omega$ , contribution of  $\varepsilon'(x)$  for the values  $x$  which are very far from the  $\omega$  is not of crucial importance. Shape of the function  $\varepsilon'(\omega)$  in some particular frequency  $\omega$  is determined by the values  $\varepsilon''(x)$  for the values  $x$  which are close to the  $\omega$ .

Relation between curves  $\varepsilon'(\omega)$  and  $\varepsilon''(x)$  for the values  $x$  in the vicinity of the  $\omega$  is determined by the Velicky, who has shown that peak of the refraction index match to the absorption

threshold, and peak of the absorption match to the drop of the refraction index.

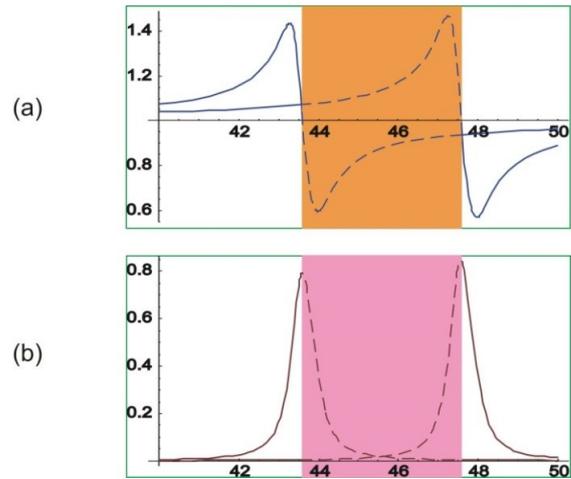


Figure 5. Refraction and absorption indices of the bulk.

These conclusions are confirmed experimentally. Maxwell has shown that dielectric permittivity of the material is equal to the square of the refraction index. Dielectric permittivity in the case of the dispersion is complex (as we have shown before), with real and imaginary parts closely related with the optical properties of the medium. Introducing complex refraction index:

$$\eta = n + i\kappa, \quad (12)$$

we will assume that it is related with complex dielectric permittivity with Maxwell equation:

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \eta^2 = n^2 - \kappa^2 + 2in\kappa. \quad (13)$$

From (13) we can determine physical meaning of real and imaginary part of complex refraction index (12), i.e.:

$$\varepsilon'(\omega) = n^2 - \kappa^2; \quad \varepsilon''(\omega) = 2n\kappa. \quad (14)$$

Based on this we can find expressions for refraction and absorption indices in next form:

$$\kappa(\omega) = \sqrt{\frac{\varepsilon'}{2} \left[ \sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2} - 1 \right]}$$

$$n(\omega) = \sqrt{\frac{\varepsilon'}{2} \left[ \sqrt{1 + \left(\frac{\varepsilon''}{\varepsilon'}\right)^2} + 1 \right]}. \quad (15)$$

On the Fig.6 are shown dependence of relative dynamic permittivity, absorption and refraction indices from the reduced energy of external e.m. field, for the 5-layered film. All graphs show this dependence for the external (boundary) crystalline planes, first inner planes and medium plane.

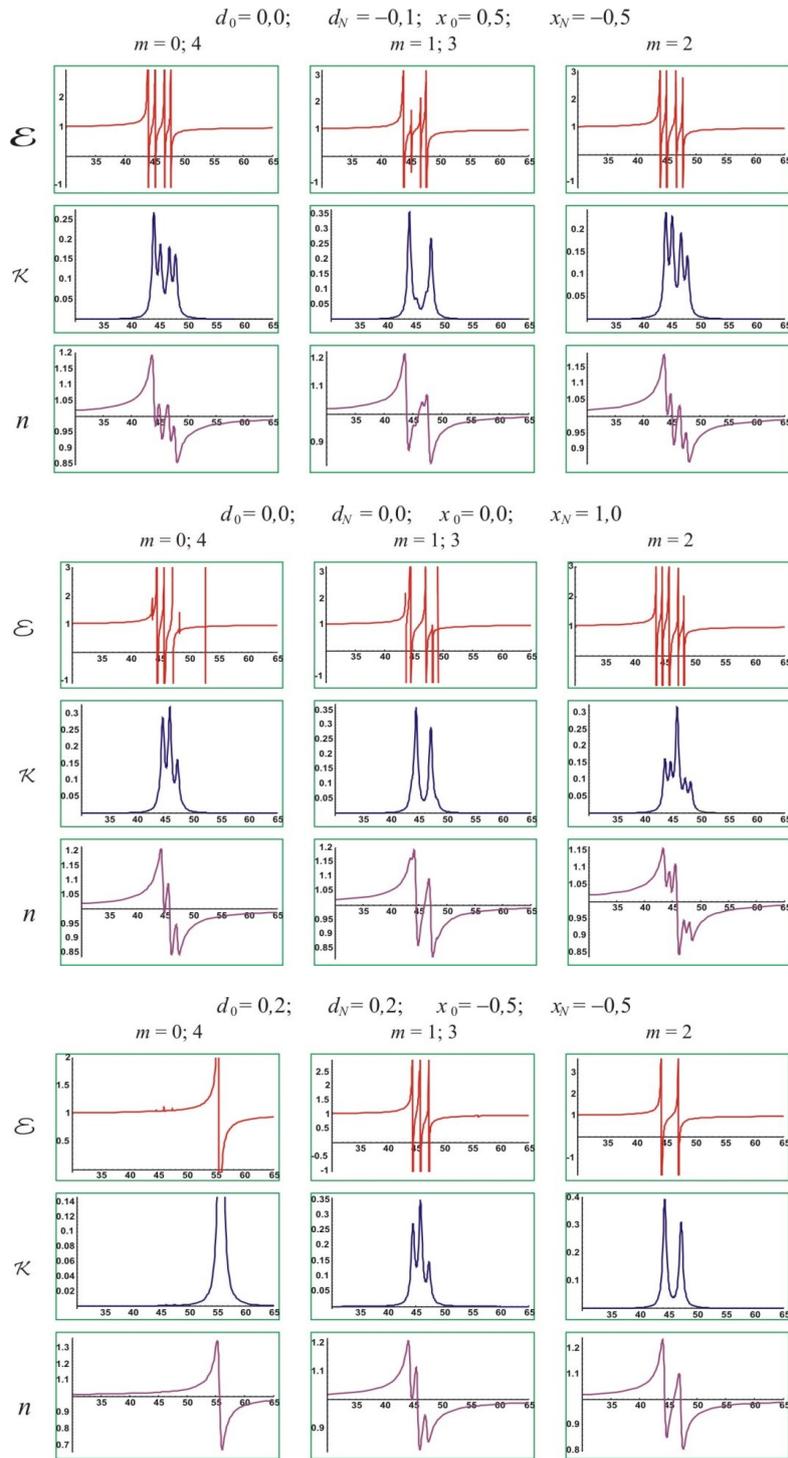


Figure 6. Relative permittivity, absorption and refraction indices for 5-layered perturbed film in dependence of relative energy .

On the first upper graphs in Fig. 6 are shown permittivity of ideal film with 4 inner atomic layers [more detail in 12]. In the second and third row are shown graphs for absorption and refraction indices in dependence of reduced frequency of external electromagnetic field for a 4-layered dielectric film when term  $\Delta$  has been changed with perturbation parameter  $d_0$  (or  $d_N$ ). One can see that number of resonant peaks

(frequencies where  $\varepsilon(\omega_r) \rightarrow \pm \infty$ ) depend on number or position of atomic plane  $n_z$  for which dielectric permittivity has been calculated, but also from values of perturbation parameters  $d_{0/N}$ . When we increase perturbation parameter, the absorption zone spreads, with the dominant resonant peak noticed only on boundary plane of the film ( $n_z = 0$  ili  $n_z \equiv N = 4$ ). This is somewhat expected result, while spectral weight

analysis shows that the probability of finding excitons is the greatest right on those planes [12]. It is easy to notice that number of resonant permittivity peaks varies with each layer, i.e. permittivity is not only frequency depended, but also layer depended and function of perturbation parameters  $x_{0/N}$ . Increasing perturbations parameters  $x_{0/N}$  absorption zone is widening to higher and lower energies, accompanied with simultaneously quenching of some resonant peaks, depending of layer (or plane) for which is permittivity calculated. This means that visibly greater impact on optical properties has  $d$ -perturbation parameter, which shifts the whole energy spectra and could make very narrow absorption, making in that way film structure some kind of a monochromatic filter. From all graphs one can see that smoothly increasing of refraction index has its breakdown on frequencies where absorption properties change (absorption index). On the frequencies where absorption index increase – refraction index decrease; where absorption indices change more rapidly (increase or decrease) are peaks of refraction indices (singularities). Those results are in good agreement with Kramer's theory, with only difference that those effects occurs on the beginning and end of absorption zone, while in film structures effects are discrete, giving quantum and very selective narrow absorption zone.

## V. CONCLUSION

There are a significant differences in dispersion law (microscopic, i.e. quantum) and dielectric response (macroscopic, but dimensionally quantum) of excitons between bulk and symmetrical ultrathin film structures. This is a consequence of dimensional limitations along one axe, but also of perturbation effects on boundary planes and layers. An energy spectrum of excitons in symmetrical ultrathin film is discrete one with a number of energy levels equal to the number of atomic planes. Increasing of energy of excitons on boundary layers, i.e. crystal nodes, moves spectrum towards higher energies (frequencies), while increasing energy transfer between boundary and first inner neighbor planes symmetrically spreads spectrum towards higher and lower energies (frequencies). There is a possibility of appearance of Tamm's (or localized) states, with probability that those states occurs significantly increase with increasing of perturbation parameters. Dielectric response of ultrathin films show properties of distinct selectivity, with appearance of resonant absorption peaks on exactly determined energies (frequencies). Number and disposition of those resonant peaks depend on number of atomic layers and perturbation parameters. These properties give advantage of film structures above bulk (which

have continual dielectric response in certain energy zone). In this sense ultrathin film structures could be used as some kind of monochromatic filters of external radiation.

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## REFERENCES

- [1] Wood K., Hammond P., Schmidt D., Wrightman S. and Andaya B., Thin Film Delivers Drugs, Biophotonics, Cambridge, 12.02.2008; (<http://www.photonics.com>)
- [2] Tringides M.C., Jatochawski M. and Bauer E., Physics Today, pp.50-54, April 2007.
- [3] Davison S.G. and Steslicka M., Basic Theory of Surface States, Clarendon Press, Oxford, 1996.
- [4] Agranovich V.M. and Ginzburg V.L., Crystaloptics with Space Dispersion and Theory of Excitons, Nauka, Moskwa, 1979.
- [5] Mirjanić D.Lj., Kozmidis-Luburić U.F., Marinković M.M., Tošić B.S., Can.J.Phys. 60, p.1838, 1982.
- [6] Rickayzen G., Green's Functions and Condensed Matter, Academic Press, London, 1980.
- [7] Mahan G., Many Particle Physics, Plenum Press, New York, 1990.
- [8] Dzialoshinski I.E. and Pitaevski L.P., Zh.eksper.teor.Fiz. 36, p. 1977, 1959.
- [9] Pelemiš S., Škipina B., Vučenović S.M., Mirjanić D.Lj. and Šetrajčić J.P., Tehnika – Novi materijali 2, p. 13, 2008.
- [10] Cottam M.G., Tilley D.R., Introduction to Surface and Superlattice Excitations, University, Cambridge, 1989.
- [11] B.Škipina, D.Lj.Mirjanić, S.M.Vučenović, J.P.Šetrajčić, I.J.Šetrajčić, A.J.Šetrajčić-Tomić, S.S.Pelemiš and B.Markoski, Selective IR Absorption in Molecular Nanofilms, *Optical Materials* **33**, 1578-1584, 2011.
- [12] S.M.Vučenović, B.V.Škipina, S.S.Pelemiš, A.J.Šetrajčić-Tomić, S.Armaković, J.P.Šetrajčić, I.J.Šetrajčić, B.Markoski, Optical Properties Analysis of Ultrathin Crystalline Structures with Broken Symmetry, *4th MolMat*, Montpellier, France, 2010.
- [13] J.P.Šetrajčić, B.Markoski, D.Rodić, S.S.Pelemiš, S.M.Vučenović, B.Škipina and D.Lj.Mirjanić, Absorption Features of Symmetric Molecular Nanofilms, *8th ICNN*, Thessaloniki (Greece), 2011.
- [14] J.P.Šetrajčić, S.S.Pelemiš, S.M.Vučenović, V.M.Zorić, S.Armaković B.Škipina and A.J.Šetrajčić, Absorption Features of Symmetric Molecular Nanofilms, Proceedings 27th MIEL, 127-130, 2010.
- [15] Pelemiš S.S., Šetrajčić J.P., Markoski B., Delić N.V. and Vučenović S.M., Selective Absorption in Twolayered Optic Films, *J.Comput.Theor.Nanosci.* 6(7), 1474-1477, 2009.