Optik 125 (2014) 2830–2834

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Some optical specificity of ultrathin crystalline films

Branko Markoski[a,1], Ana J. Šetrajčić-Tomić[b,2], Dragana Rodić[c,3], Igor J. Šetrajčić[c,3], Svetlana Pelemiš[d,4], Jovan P. Šetrajčić[c,*]

[a] University of Novi Sad, Technical Faculty "M. Pupin" Zrenjanin, Đ. Đakovića bb, 23000 Zrenjanin, Vojvodina, Serbia
[b] University of Novi Sad, Faculty of Medicine, Department of Pharmacy, Hajduk Veljkova 3, 21000 Novi Sad, Vojvodina, Serbia
[c] University of Novi Sad, Faculty of Sciences, Department of Physics, Trg D. Obradovića 4, 21000 Novi Sad, Vojvodina, Serbia
[d] University of East Sarajevo, Faculty of Technology, Zvornik, Karakaj bb, 75400 Zvornik, Republic of Srpska, Bosnia and Herzegovina

ARTICLE INFO

Article history:
Received 12 June 2013
Accepted 16 November 2013

Keywords:
Ultrathin film
Excitons
Dispersion law

ABSTRACT

The changes of optical properties under boundary presence in molecular crystal nanofilm were theoretically investigated in this work. The dispersion law and states of excitons as well as their space distribution along boundary direction have been determined using adjusted Green's function method and also by combined analytical and numerical calculations. On the basis of real and imaginary part of relative permittivity, both absorption and refraction indices were determined, and the influences of boundary parameters on occurrence of a very selective and strictly discrete absorption were analyzed.

1. Excitons in molecular structures

In this theoretical research of optical properties of nanostructure materials[5] we have to start from the assumption that excitons are generated in materials as response on the external electromagnetic field [1]. Although excitons are not the only (quasi) particles that can be found in nanostructures when external electromagnetic field is turned on, this statement is satisfactorily correct if we use molecular crystals [2]. Following this fact, we would restrict our research on dielectric (non-conductive) molecular crystalline materials, where standard excitons Hamiltonian include Pauli-operators with unsuitable statistic and therefore we would have to cross onto Bose statistics [1–3] in lowest approximation[6]:

$$H = \sum_{\vec{n}} \Delta_{\vec{n}} B_{\vec{n}}^{+} B_{\vec{n}} + \sum_{\vec{n},\vec{m}} X_{\vec{n}\vec{m}} B_{\vec{n}}^{+} B_{\vec{m}}, \tag{1.1}$$

in further calculus we would use Green's function method [5] and corresponding equation of motion:

$$i\hbar \frac{d}{dt} G_{\vec{n}\vec{m}}(t) = i\hbar\delta(t)\delta_{\vec{n}\vec{m}} + \Delta_{\vec{n}} G_{\vec{n}\vec{m}}(t) + \sum_{\vec{l}} X_{\vec{n}\vec{l}} G_{\vec{l}\vec{m}}(t);\ G_{\vec{n}\vec{m}}(t) \equiv \left\langle \left\langle B_{\vec{n}}(t) \middle| B_{\vec{m}}^{+}(0) \right\rangle \right\rangle. \tag{1.2}$$

In approximation of the nearest neighbor, but including dimensional restrictions related to configuration and internal organization of nanostructure, in particular we would observe ultrathin films. The next step is transition from direct space to k-space, i.e., performing the time and space Fourier's transformations [3,5].

* Corresponding author. Tel.: +381 21 455 318; fax: +381 21 455 318.
E-mail addresses: markonins@yahoo.com (B. Markoski), setrajcic@open.telekom.rs (A.J. Šetrajčić-Tomić), rodic.dragana5@gmaim.com (D. Rodić), igor.setrajcic@df.uns.ac.rs (I.J. Šetrajčić), alannica@gmail.com (S. Pelemiš), jovan.setrajcic@df.uns.ac.rs (J.P. Šetrajčić).
[1] Tel.: +381 23 550 515; fax: +381 23 550 515.
[2] Tel.: +381 21 420 677; fax: +381 21 420 677.
[3] Tel.: +381 21 455 318; fax: +381 21 455 318.
[4] Tel.: +387 56 261 190; fax: +387 56 261 190.
[5] Preliminary results of this work are presented at Annual YUCOMAT Conferences, Herceg Novi – Montenegro, Sept. 2010–1012.

[6] The basic idea of this research is to investigate the influence of boundaries (boundary conditions) on the fundamental properties of nano-thin molecular film. Therefore, we decided to use such rough approximation, but we were sure that our calculation of the *internal deformations of optically excited sites and the respective elongations of internal vibrations* will not negatively affect finding of contribution *quantum size effects and existence of specific boundary conditions on film surface layers* although it would give better and more realistic insight into optical properties. In addition, we are still not familiar with how to model and take into account all of these effects in nano-confined structures (for balk-structures that is already discovered, for example in [4]). In any case, that remains for us as a very serious scientific task in near future.

0030-4026/$ – see front matter © 2014 Elsevier GmbH. All rights reserved.
http://dx.doi.org/10.1016/j.ijleo.2014.01.006

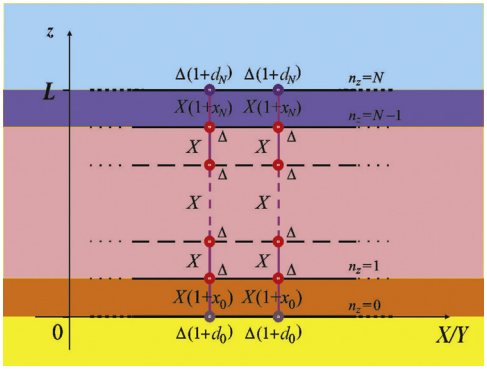

Fig. 1. Model of exciton *N*-layered film-structure.

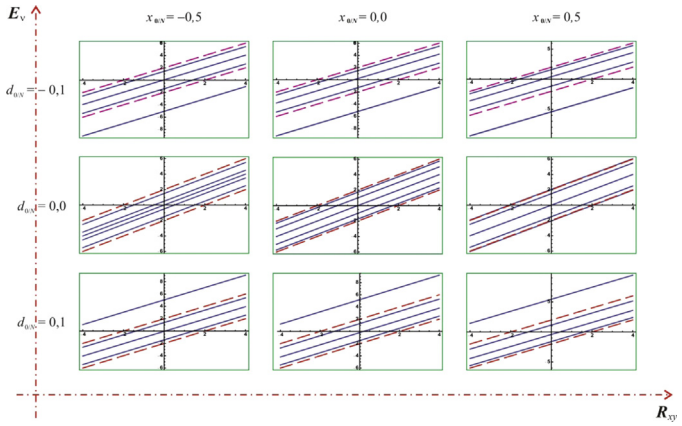

Fig. 2. Exciton dispersion law in 4-layered film-structure.
On all graphs, the reduced exciton energies E_ν – from (4) are given by solid line in function on dimensionless function $R_{xy} \in [-4,+4]$, for three (different) characteristic values of boundary parameters: $d = -0{,}1;\ 0{,}0;\ +0{,}1$ and $x = -0{,}5;\ 0{,}0;\ +0{,}5$. With dashed lines are presented boundaries for continuous energy zone in bulk crystals.

Advantage of this transition is direct and elegant calculation of energy dispersion law.

2. Dispersion law of excitons in ultrathin films

We have calculated energy dispersion law for excitons in nanostructure sample – the ultrathin film consists of up to 10 parallel layers of molecular crystalline planes, with significant influence of boundaries, which are represented through two kind of exciton perturbations – one is localized on the site of the molecule, and the second is energy transfer between boundary plane and the first internal neighbor plane. We will indicate with Δ exciton energy on the site of the molecule, and with $d_{0/N}$ perturbation on that energy, in the first/last plane (Fig. 1).

Similarly, we will indicate with X energy transfer between neighbor planes and with $x_{0/N}$ perturbation on that energy, between the boundary planes and their first neighbor planes (i.e., it is denoting the perturbation of energy transfer of excitons in boundary layers):

$$\begin{aligned}\Delta_{\vec{n}} &\equiv \Delta[1+(d_0\delta_{n_z,0}+d_N\delta_{n_z,N})],\\ X_{\vec{n},\vec{n}+\vec{\lambda}} &\equiv X[1+(x_0\delta_{n_z,0}+x_N\delta_{n_z,N-1})],\\ X_{\vec{n},\vec{n}-\vec{\lambda}} &\equiv X[1+(x_0\delta_{n_z,1}+x_N\delta_{n_z,N})]\end{aligned} \tag{2}$$

Using above explained Green's function procedure [6], where we must perform full time and partial space Fourier-transformation[7], we have obtained system of $N+1$ algebraic difference equations for $N+1$ unknown Green's function, where $N+1$ denote number of atomic planes in ultrathin films:

$$\begin{aligned}&G_{n_z,m_z}\left[\rho-\frac{\Delta}{|X|}(d_0\delta_{n_z,0}+d_N\delta_{n_z,N})\right]+G_{n_z-1,m_z}[1+(x_0\delta_{n_z,0}+x_N\delta_{n_z,N-1})]+\\ &+G_{n_z+1,m_z}[1+(x_0\delta_{n_z,1}+x_N\delta_{n_z,N})]=\frac{i\hbar}{2\pi|X|}\delta_{n_z,m_z},\\ &\rho=\frac{\hbar\omega-\Delta}{|X|}+2(\cos ak_x+\cos ak_y).\end{aligned} \tag{2.1}$$

To calculate energy dispersion law for excitons in ultrathin films, it is sufficient to resolve determinant of the system, because poles of the Green's function define exciton energies, which leads to equalizing determinant of the system with zero [5–7]:

$$\begin{aligned}&E_\nu=\frac{\hbar\omega-\Delta}{|X|}\equiv R_{xy}-\rho_\nu,\ R_{xy}\equiv 2(\cos ak_x+\cos ak_y),\\ &\nu=1,2,\ldots,N+1.\end{aligned} \tag{2.2}$$

Fig. 2 shows non-dimensional form of the exciton energy law for 4-layered film ($N=4$), i.e., 5-planed film, depending on different values of perturbation parameters ($d_{0/N}$, $x_{0/N}$). Here and further as well, we will observe ultrathin film with symmetrical boundaries when: $d_0 = d_N \equiv d_i$ and $x_0 = x_N \equiv x$. This case corresponds to the nanofilm obtained by doping in a matrix, thus substrate and external environment are practically the same (detailed explanation is given in [8]).

The crucial result is discreteness of the exciton energies, which is direct consequence of the ultra-low dimensionality of the system, well known as quantum size effects. However, the distribution of discrete lines is a consequence of changed boundary conditions on the surface layers of the film. One can see that sufficient small decrease or increase in d-perturbation (less to 10%) bring two energy levels out of the bulk zone and that only large positive x-perturbation (up to 50%) could bring two energy levels.[8]

3. Spatial distribution of exciton states in film-structure

To obtain spectral weights, i.e., probability of finding exciton states in ultrathin films, we must calculate Green's functions from the system of equations. This could be done if we solve system in matrix form (it is given in detail in [6]). Green's functions are roots of the matrix equations, and they are in general case multiplex:

$$G_{n_z}=-\frac{i\hbar}{2\pi|X|}\sum_{\nu=1}^{N+1}\frac{g_{n_z}(\rho_\nu)}{\rho-\rho_\nu} \tag{3.1}$$

After performing factorization, in the numerator $g_{n_z}(\rho_\nu)$ arise spectral weights of excitons in certain type of nanostructures [7–9]. In the ultrathin films, distribution of excitons per molecular planes with particular energy is highly dependable on values of perturbation parameters (d and x), and in [7] it is shown that the localized exciton states– those with the highest energy, most likely located just on the border surfaces or in the boundary layer film. This fact has resulted in changing the optical properties of ultrathin film structures.

[7] Partial space Fourier's transform is performed while we assume that film is finite along z-axe, and practically infinite along other two dimensions.

[8] Those states are well known as Tamm's or localized states [1,2].