Effect of Langmuir coating on the localization of excitonic polarization in CdS surface layer

K A Korolkova¹, V R Novak² and A V Sel’kin¹³
¹Solid State Spectroscopy Laboratory, Ioffe Institute, 26 Polytekhnicheskaya, St-Petersburg 194021, Russian Federation
²NT-MDT Spectrum Instruments LTD, Moscow, Zelenograd, 124460, Russian Federation
³Solid State Physics Department, Saint-Petersburg State University, Ulyanovskaya 1, Peterhof 198504, Russian Federation
e-mail: ksenia.korolikova@gmail.com

Abstract. Low temperature (T=2K) optical reflection spectra have been studied for the organic-semiconductor structures prepared by deposition of Langmuir-Blodgett films on CdS surface. The spectra are measured in the resonant spectral range of the $A_{n=1}$ exciton state in CdS. Theoretical analysis of the spectra is carried out with an account of the spatial dispersion effects and the exciton-free surface “dead” layer. The conclusion has been drawn of the interface localization of the Wannier-Mott exciton due to organic film deposition on the crystal surface.

1. Introduction

Over the past few decades, there has been a steady interest in development and improvement of optoelectronic devices based on organic-semiconductor structures [1,2]. A number of researches have been reported in the literature [3-6] which consider such “hybrid” objects in light of the resonant interface interaction between the Frenkel exciton in organic material and the Wannier-Mott exciton in semiconductor. It was pointed [6,7] that at an optical excitation of the contacting organic and semiconductor media a hybrid state of the two type excitons can be created.

In the present work, we studied the excitonic specular reflection spectra of CdS crystals covered by Langmuir-Blodgett films, both experimentally (T=2K) and theoretically. The planar organic-semiconductor structures were prepared by deposition of mono- and multilayer films on the single cadmium sulfide plates (CdS substrates). The spectra under study are found to strongly depend on the number of organic monolayers deposited on the crystal surface. Appropriate theoretical analysis was carried out making use of a multilayer model for light reflection taking into account the near-surface crystal “dead” layer for excitons [8] and spatial dispersion effects. A technique based on the boundary conditions (BC) statement including Maxwell’s BC and additional boundary conditions (ABC) was developed. For ABC we used generalized additional boundary conditions (GABC) which are written as the vanishing of a linear combination of the excitonic polarization and its spatial derivative at the dead layer inner interface. It was found that standard (classical) Pekar’s ABC don’t allow one to reproduce in calculations the most significant spectral features observed experimentally in reflectivity.

2. Experimental results and theory
The organic monolayer Langmuir-Blodgett films layered on CdS crystal plates were prepared from 4-nitro-4'-N-octadecylaminobenzene (NAB), the thickness of every monolayer (ML) being about 2.7 nm. The CdS crystals playing the role of substrates were pre-selected so that their resonance reflection spectra in the region of the exciton state \( A_{n=1} \) were well described by the standard model of Hopfield and Thomas (Pekar’s ABC on the inner surface of the near-surface dead layer) [8]. Reflection spectra were measured for the samples placed in a cryostat with pumped vapors of liquid helium \((T=2K)\) in the \(\sim 2545-2560\) meV range.

The geometry of the reflection experiment is schematically shown in figure 1. Such a geometry corresponds to oblique incidence of \( p \)-polarized light at an angle \( \theta \) with the electric field vector \( E \) being perpendicular to the optical crystal axis \( C_6 \) which in turn is parallel to the crystal surface plane. The electric vectors \( E_0 \) and \( E_p \) for incident and reflected light, respectively, lie in the \( XZ \)-plane of incidence. An organic film \((Z \leq Z \leq Z)\) of the thickness \( L_F \) covers a semi-infinite semiconductor crystal \((Z \geq Z)\) with the exciton-free dead layer \((Z \leq Z \leq Z)\) of the \( L_{DL} \) thickness. In figure 1, the organic NAB film is implied (as an example) to consist only of two monolayers. The space region \( Z \leq Z \) belongs to outer medium of the permittivity being equal to unity.

![Figure 1. Geometry of the reflection experiment and the model structure under consideration.](image)

It is important for our consideration that configuration of the polarization \( E \perp C_6 \) is used because for this polarization the optical transition to the exciton state \( A_{n=1} \) does allowed in dipole approximation whereas for \( E \parallel C_6 \) the transition is forbidden. As for optical properties of the NAB film, it is worth to note that the film exhibits rather high absorptivity in the relatively wide spectral range from \( \sim 2.3 \) to \( 3.0\) eV with the absorption maximum centered at about 2.7 eV. In figure 2, the experimental specular reflection spectrum of CdS with the film thickness of \( L_F = 6 \) ML is presented (1 - open circles). The spectrum was measured at the angle of incidence \( \theta = 45^\circ \). For comparison, we show here the result of theoretical calculation (2 – dashed line) based on the Hopfield - Thomas classical approach [8] with an additional account of the NAB film covering the CdS surface. As seen from such calculation, the reflection contour 2 demonstrates a typical shape which is observed usually for more perfect as-grown CdS crystals. The reflection coefficient \( R \) first increases smoothly with increasing frequency reaching a maximum value at about 2553 meV. Further, as the frequency increases, there is a rapid decrease in \( R \).
and an additional (anomalous) structure is formed in the region of the main reflection minimum, against the background of which a narrow reflection peak (spike) appears. The spectral position of the spike at small angles of incidence practically coincides with the frequency $\omega_L$ for the longitudinal exciton with the wavevector $k = 0$.

Such a behavior of the theoretical curve describes, at least qualitatively, all the spectral features registered in the short-wave part of the experimental spectrum to the right of main maximum. However, to the left of this maximum (on the long-wave shoulder of the spectrum) one can select a remarkable difference between theory and experiment. Namely, an additional maximum in the reflection experiment is manifested at the frequency $\omega_s \approx 2548$ meV whereas the conventional theoretical model does not allow such a maximum to be revealed.

In order to describe theoretically our experimental data we addressed the problem by generalizing ABC when writing them for the excitonic polarization $P$ at the interface $Z = Z_1$ (as figure 1 indicates) in the form (see also [9])

$$
\left( P(\omega, r) + \frac{1}{\eta k_0} \frac{\partial P(\omega, r)}{\partial z} \right)_{z = z_1} = 0
$$

where $\eta$ is some complex-valued phenomenological dimensionless coefficient, $k_0 = \omega / c$ is the wave number of light in vacuum.

Making use of the generalized boundary conditions (GABC) in the form of equation (1) it is possible to find a complex value $\eta = 24 + 5i$ that allows us (as shows the curve 3 in figure 2) to reproduce theoretically all the principal peculiarities in the shape of the reflection contour within the spectral range of interest. When computing the spectra 2 and 3 we took the same values of parameters for a bulk CdS crystal: $\omega_0 = 2552.4$ meV, $\omega_{LT} = 2.0$ meV, $\Gamma = 0.15$ meV, $M = 0.9 m_0$, $\epsilon_b = 9.3$, where $\omega_0$ is the resonant frequency of the $A_{n=1}$ exciton state, $\omega_{LT} = \omega_L - \omega_0$ is the longitudinal-transverse splitting, $\Gamma$ is the excitonic damping constant, $M$ is the translational effective mass of an exciton expressed through the mass $m_0$ of the free electron, and $\epsilon_b$ is the background permittivity. The thickness $L_{DL}$ of

![Figure 2. Experimental (1 – open circles) reflection spectrum of CdS covered by organic six monolayer NAB-film as compared to theoretical (2 – dashed and 3 – solid lines) calculations at the angle of incidence $\theta = 45^0$ for p-polarized $E \perp C_6$ light in the vicinity of the excitonic resonance $A_{n=1}$ ; 2 – Pekar’s ABC, 3 – generalized ABC.](image)
the exciton-free dead layer was taken to be equal to 50 nm. As to the organic NAB film, its thickness in
the case of the curve 3 corresponds to 6 monolayers (1ML=2.7 nm), its permittivity $\varepsilon_f$ equals 1.89+2i.

For better understanding a physical sense of the $\eta$ parameter, let us consider the more simple case of
normal incidence of light when only two transverse eigen modes are exited in the bulk on a certain
frequency $\omega$. These modes are characterized by the refractive indices $n_\nu = k_{\nu z} / k_0$ ($\nu = 1, 2$) and can
be written in the form of the plane waves

$$P^{(\nu)}(\omega, z) = P_\nu \cdot \exp(ik_\nu n_\nu z)$$

Then the GABC (1) gives for the amplitude ratio at

$$\frac{P_2}{P_1} = -\frac{\sqrt{\omega_0 - \omega_s} + \sqrt{\omega_0 - \omega}}{\omega - \omega_s} \left( \sqrt{\omega_0 - \omega_s} + i \sqrt{\varepsilon_0 \omega_M \omega_s - \omega_0 \omega} \right)$$

where

$$\omega_s \equiv \omega_0 - \omega_M \eta^2$$

with $\omega_M = \hbar k_0^2 / 2M$.

As follows from equations (3-4), there exists a frequency $\omega_s$ (depending on $\eta$) which corresponds
to the pole of the $P_2 / P_1$ ratio. In other words, at the frequency $\omega_s$ the mode $\nu = 1$ is fully cancelled
but the mode $\nu = 2$ is excited being at $\eta^2 > 0$ evanescent one because $\omega_s < \omega_L$. So, at the frequency
$\omega_s$ a strong localization of excitonic polarization occurs at the interface $z = z_i$ and a high reflectance
(ideally of 100%) can be expected at this frequency.

If the parameter $\eta$ is considered as complex-valued one, the frequency $\omega_s$ becomes complex, as
well. Then we can associate the imaginary part of $\omega_s$ with the lifetime $\tau_s$ of the interface localized
state of an exciton characterized by some resonant frequency determined by the real part of $\omega_s$.

In terms of the reciprocal lifetime, i.e. the damping constant $\Gamma_s = \tau_s^{-1}$, the relation (4) at sufficiently
small values of $\Gamma_s$ gives

$$\text{Re} \eta \approx \left[ (\omega_0 - \omega_s) / \omega_M \right]^{1/2}$$

$$\text{Im} \eta \approx \Gamma_s / 4 \left[ \omega_M (\omega_0 - \omega_s) \right]^{1/2}$$

where the frequency $\omega_s$ is considered as real one.

So, as seen from equations (5-6), the real part of $\eta$ is directly associated with the resonance frequency
$\omega_s$ of the localized state and the imaginary part of $\eta$ is directly determined by the damping constant
$\Gamma_s$. In other words, $\text{Re} \eta$ is associated with the spectral position of the additional long-wave maximum
of reflectivity, whereas $\text{Im} \eta$ determines its spectral broadening. With increasing $\text{Re} \eta$ the maximum
shifts to the long-wave side, whereas increasing $\text{Im} \eta$ gives rise to the broadening. As a result of fitting
the theoretical curves to the experimental data, the parameter $\eta = 24 + 5i$ entering GABC (1) has been
found, which corresponds to $\omega_s = 2548.2$ meV and $\Gamma_s = 1.02$ meV.

For the discussed localization of excitonic polarization, the choice of a specific angle of incidence is
not critical. The effect of the organic film thickness on the reflection spectrum shape at different angles
of incidence is noticeable and is quite expected. The measurements at $\theta = 45^\circ$ are presented here due
to considerations of experimental convenience, and, on the other hand, to the possibility of analyzing
the spectra in the framework of the GABC for the case of oblique incidence of light when along with transverse polaritons one needs to take account longitudinal exciton states.

3. Conclusion

Low temperature reflectance spectra of semiconductor CdS crystals covered with organic films are remarkable sensitive to the film thickness and demonstrate the peculiarities that are not described satisfactory in the framework of the standard Pekar-Hopfield theory based on Pekar’s additional boundary conditions (ABC) and the exciton-free “dead’ layer model. An additional reflectance peak is observed on the low-frequency shoulder of the reflection counter formed by the lowest Wannier-Mott exciton state in CdS. To understand the nature of appearance of the extra spectral features registered we developed a theory considering the generalized ABC (GABC) which look as vanishing a linear combination of the excitonic polarization and its spatial derivative at the interface between the bulk crystal and exciton-free “dead’ layer.

The parameters of GABC are shown to determine conditions for a strong near-surface localization of the excitonic polarization. Such localization corresponds to specific states of the Wannier-Mott exciton with a certain eigen frequency and lifetime depending on the GABC parameter values. Since the Langmuir films used are characterized by a noticeable absorption in the vicinity of the resonant optical transition to the considered exciton state of CdS crystal, it is very likely that the Frenkel molecular exciton in the organic film and Wannier-Mott exciton in the semiconductor crystal can create a hybrid state at the interface between the organic and semiconductor materials.

4. References

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