

Optical spectroscopy of near-surface excitonic states

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We have studied the low temperature excitonic reflectance and luminescence spectra of CdS_{1-x}Se_x solid solution with a near-surface excitonic potential well formed by excessive Se. The reflectance spectra were obtained at different angles of incidence for both- and *p*-polarization components of light. New striking spectral features due to exciton confinement and quantization in the surface region were observed. For various samples, the generalized Morse surface potential was proved to be a good approximation in describing the experimental data. It is shown that the resonance excitonic luminescence is largely governed by the emission from excitations localized in the well.

Keywords: exciton, reflectance, luminescence

Excitonic reflectance spectroscopy is known to be a widely used and powerful tool of optical spectroscopy in studying electronic energy states of solids. Excitonic reflectance spectra of light are very sensitive to small changes of material properties in the surface regions within the thickness of the order of exciton-polariton free pass length below the surface, that is, tenth of micron. In most cases, just such near-surface regions contain inhomogeneous transition layers which strongly affect experimental reflectance spectra. Therefore, the excitonic reflectance spectra can be successfully employed in characterizing optical and structural properties of the near-surface region of solid state materials [1-3].

In this paper, a study has been made of low temperature excitonic reflectance and luminescence spectra of CdS_{1-x}Se_x solid solution with near-surface excitonic potential wells formed by excess of Se. A sample growth technique was used which allowed us to modify coordinate dependence of the ground state energy and the damping parameter of an exciton along the normal to the plane surface of a crystalline plate. The spectra were obtained at different angles of incidence for both *s*- and *p*-polarization components of light.

One of the non-trivial problems when analyzing excitonic reflectance spectra from a planar inhomogeneous medium is associated with the spatial dispersion which is due to the non-local character of the material equation. Within the adiabatic approximation, when the excitonic potential $V(Z)$ is a rather smooth function of the normal-

to-surface *Z*-coordinate of the exciton center of mass, the relation between the excitonic polarization \mathbf{P} and electric field \mathbf{E} at the light frequency ω near the bulk resonant frequency ω_T is given by (see, e.g., [4,5])

$$\left(-\frac{\hbar\omega}{M}\nabla_{\mathbf{R}}^2 + \omega_T^2 - \omega^2 - i\omega_T\Gamma_0 + \frac{2\omega_T}{\hbar}V^*(Z) \right) \mathbf{P}(\mathbf{R}) = \mathbf{b}_0\omega_T^2\mathbf{E}(\mathbf{R}), \quad (1)$$

where M is the effective mass of exciton, Γ_0 is its bulk damping constant (reciprocal life time in a quantum state), \mathbf{b}_0 is the static polarizability due to the excitonic contribution, $\mathbf{R}(X,Y,Z)$ is the excitonic center of mass coordinate. The surface potential $V=V'+iV''$ is, in general, a complex function with the real part $V'(Z)$ describing the coordinate dependence of the local resonant energy of exciton and with the imaginary part $V''(Z)$, which determines a *Z* dependent contribution to the damping parameter

$$\Gamma(Z) = 2V''(Z)/\hbar.$$

In order to analyze the experimental reflectance spectra obtained, we made use of the calculation technique [4] generalized to the case of obliquely incident light. The main idea, following [1], is based on the stepwise approximation of a smooth adiabatic potential (see Fig.1, a

chematic curve $V'(Z)$. This means, that the real medium is approximated by a multi-layer one.

Fig.1 shows on an enlarged scale two adjacent homogeneous layers, α and β . In each of the layers six possible modes of the same frequency ω can be excited by outer light incident at an angle \mathbf{j} in p -polarization: three of them, $1^+, 2^+$ (transverse) and 3^+ (longitudinal), propagate into the bulk, and other three, $1^-, 2^-$ (transverse) and 3^- (longitudinal) go to the surface. In the case of s -polarization, only four transverse modes, $1^+, 2^+, 1^-$ and 2^- can be excited in each of the layers. The amplitudes of the reflected, i^- , and incident, j^+ , waves ($i, j=1, 2, 3$) on every boundary α ($\alpha=1, \dots, N$, where N is the total number of interfaces) are related by the reflection coefficients r_{ij}^a .

The tangential components of the electric field vector \mathbf{E} at every interface α obey boundary conditions: Two of them (Maxwell's ones) follow from the continuity of the tangential components of the electric and magnetic field vectors, the other four (additional boundary conditions [5]) correspond to the continuity of the excitonic polarization field \mathbf{P} and its derivative $\partial\mathbf{P}/\partial Z$. It is enough to use these boundary conditions in order to express the reflection coefficients r_{ij}^a on the boundary \mathbf{a} through the coefficients r_{ij}^b on the next boundary \mathbf{b} . So, calculating the reflection coefficients on the interface between the bulk and the near-surface transition layer and In Fig.2 we show a reflectance spectrum (c) of CdSSe solid solution ($T=2K, \mathbf{E}\perp\mathbf{C}$) with a small content of excessive Se which forms, due to its inhomogeneous distribution along Z axis, a near-surface potential well. The spectrum is recorded in the vicinity of $A(n=1)$ exciton resonance frequency at the near-normal angle of incidence $\mathbf{j} = 8^\circ$. As an approximation we considered a two exponent function for the real part of the potential assuming the imaginary part to be exponentially increased towards the surface:

$$V(Z) = U_1 \exp[-(Z-Z_1)/L_1] - U_2 \exp[-(Z-Z_2)/L_2] + iU_3 \exp[-(Z-Z_3)/L_3] \quad (2)$$

The best fit parameter values corresponding to the theoretical reflectance curve (b) and potential curve (a) are as follows: $U_1 = U_2 = 0.903$ meV, $U_3 = 0.53$ meV, $L_1 = 12.9$ nm, $L_2 = 41.8$ nm, $L_3 = 99.3$ nm, $Z_1 = 88.9$ nm, $Z_2 = 19.6$ nm, $Z_3 = 42.5$ nm; $\hbar\omega_T = 2543.7$ meV, $\mathbf{b}_0 = 1.173 \cdot 10^{-3}$, $\hbar\Gamma_0 = 0.105$ meV. The background dielectric constant $\epsilon_b = 9.4$ was taken to be the same for the transition layer and the bulk. The number of elementary homogeneous layers was chosen to be $N=100$. A comparison of the experimental reflectance data with the theoretical ones for oblique incidence ($\phi=45^\circ, 60^\circ$) in p -

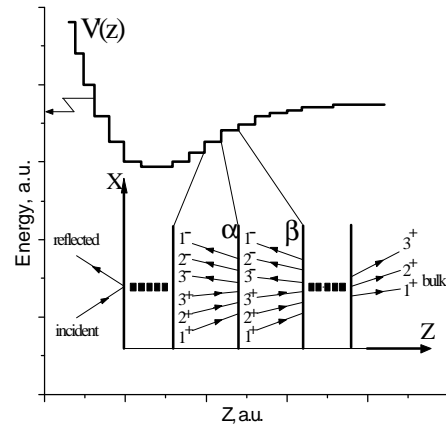


Fig. 1. Multistep model for the near-surface potential well

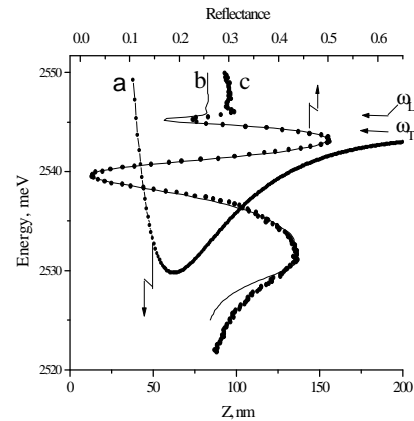


Fig. 2. The experimental excitonic reflectance spectrum (c) of CdSSe solid solution with small content of Se for $T=2K$ at the near-normal angle of incidence $\phi=8$ degrees (p -polarization, $\mathbf{E}\perp\mathbf{C}$) as compared to the theoretical one (b) calculated with the model of the two-exponent surface potential (a).

and s -polarization of light is given in Fig.3, the parameter values being the same as for the near-normal incidence.

We can see that there is a rather good agreement between the experimental and theoretical results. Hence, the potential chosen gives a good approximation for the real near-surface excitonic potential in the sample studied.

Fig.4 demonstrates the luminescence spectrum of the sample under study together with the reflectance data at near-normal incidence. The resonant frequencies of A- and B-excitons are marked by vertical arrows on the reflectance spectrum. In the luminescence spectrum two prominent structures A_w and A'_w are observed which can be related to emission of the bulk free excitons (exciton-polaritons) and excitons localized by potential fluctuations in the near-surface region (see, e.g. [3]). Unfortunately, rather high values of the imaginary part of the excitonic potential in the sample studied do not allow us to observe

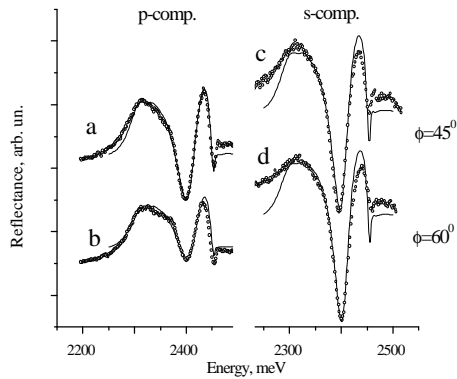


Fig. 3. The experimental reflectance spectra of CdSSe ($T=2K$) as compared to the theoretical ones at oblique incidence of light with p - and s -polarizations: $\phi=45$ degrees (a,c), $\phi=60$ degrees (b,d), \mathbf{E} being perpendicular to \mathbf{C} . The parameter values of the two-exponent potential (curve “a” in Fig. 1) were used.

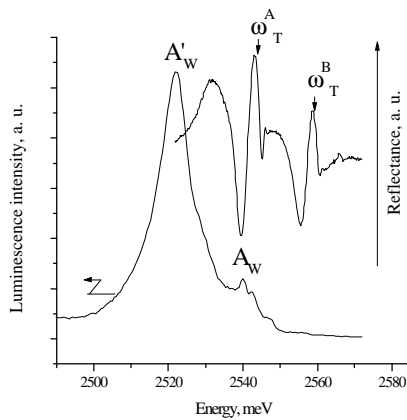


Fig. 4. The luminescence and reflectance spectra of CdSSe ($T=2K$) at near-normal incidence of light in p -polarization, \mathbf{E} being perpendicular to \mathbf{C} . ω_T^A and ω_T^B are the transverse resonant frequencies of A - and B -excitons, respectively. A_W structure in the luminescence spectrum corresponds to the bulk $A(n=1)$ resonant polariton emission, A'_W is supposed to be due to emission from $A(n=1)$ -excitons localized by the random part of the near-surface potential.

experimentally very interesting spectral peculiarities due to quantization of excitonic states in the potential well.

In order to show a possible manifestation of the quantized excitonic levels we computed with reflectance transfer method the reflectance spectra at low and high values of the exciton damping, making use of the Morse potential [6]. The parameter values of this potential were chosen in such a way that it corresponds more closely to the two-exponent potential (2) found above from the analysis of the experimental spectra. These values are: $U_2=2U_1$, $U_1=14.6$ meV, $L_2=2L_1$, $L_1=25$ nm, $Z_1=Z_2=60$ nm. The corresponding potential curve (a) with

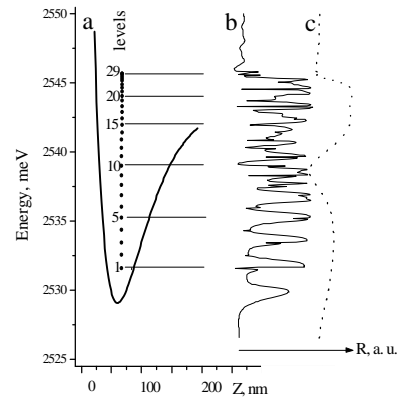


Fig. 5. The model Morse near-surface excitonic potential (a) close to the potential from Fig. 1 and the corresponding theoretical reflectance spectra for p -polarization at $\phi=45$ degrees: b – low damping, c – high damping. Longitudinal exciton quantized energy levels are marked and numbered.

calculated positions of quantized energy levels (1 to 29) for a longitudinal exciton is depicted in Fig.5.

The potential curve is compared with the reflectance spectra computed for the angle of incidence $\phi=45^\circ$ at low (b, $U_3=\hbar\Gamma_0/2$ d=0.001 meV, $L_3=100$ nm, $Z_3=19.6$ nm) and high (c, $U_3=\hbar\Gamma_0/2=0.051$ meV, $L_3=34.6$ nm, $Z_3=19.6$ nm) exciton damping. It is clearly seen that sharp reflectance minima of the curve “b” (low damping) are located exactly at the points where the energy states of the longitudinal exciton exist. At the same time, at high damping (the curve “c”) the quantization structure disappears in reflectance and only main features due to classical behaviour of the particle near the surface are manifested.

Acknowledgements

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References

- [1] A.E.Cherednichenko and V.A.Kiselev, Progress.in Surface Science **36**, No.3, 177 (1991).
- [2] A.S. Batyrev, B.V. Novikov, A.V. Sel'kin. JETP Lett. **61**, No.10, 809 (1995).
- [3] A.S. Batyrev, B.V. Novikov, A.V. Sel'kin, L.N.Tenishev, JETP Lett. **62**, No.10, 408 (1995).
- [4] A.V. Sel'kin, Vestnik SPbGU (St.Petersburg State University, Russia), Ser.4, **2**, No.11, 87 (1996).
- [5] P. Halevi, in *Spatial dispersion in solid and plasmas*, ed. by P.Halevi, Chap. 6 (Elsevier, Amsterdam, 1992).
- [6] F.Pérez-Rodríguez and P.Halevi, Phys.Rev. B **45**, No.20, 11854 (1992); Phys. Rev. B **53**, No.15, 10086 (1996).