Exciton localization on a semiconductor surface

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Complex excitonic light reflection spectra can contain information on a new phenomenon: localization of excitons in the space charge layer. The surface potential of the exciton leading to localization is proposed for a specific spectrum and a reflection spectrum which reproduces all observed characteristics is calculated.

The presence of a space charge layer (SCL) on the surface of a semiconductor which is characterized by a different charge state and, in general, by an impurity concentration different from that of the bulk leads to the fact that the parameters of the exciton are functions of the distance from the surface. This circumstance can lead, in particular, to localization of excitons in SCL, which, depending on the specific characteristics of the layer, has numerous manifestations in excitonic reflection spectra.[1–3] In this paper we shall discuss one of the most complex excitonic light reflection contours (ELRC), the analysis of which indicates localization of excitons on the semiconductor surface.

The mechanism involving the attraction of excitons to a surface, which has been thoroughly studied, is based on the interaction with the average electric field in the SCL. This mechanism was first examined by Gribnikov and Rashba.[4] If the Stark well arising due to this interaction is deep enough,[2] it may be expected that discrete exciton levels will be present in it and that these levels will be manifested in the optical spectra.[1)]

But, as it happened, there are ELRC which cannot be explained within the framework of this simple model. Examples of such spectra are shown in Fig. 1. The spectra were obtained with thin plates of single crystals of CdSe at $T = 4.2$ K. Analogous spectra have been recorded for CdS.

We shall list the characteristic peculiarities of the spectra under discussion. 1) The main reflection peak in the starting state exhibits a fine structure (Fig. 1a). This structure changes considerably under surface-sensitive electron bombardment (EB) (Fig. 1b).[3] 2) In the region of the frequency of the longitudinal exciton $\omega_L = 14730\ \mathrm{cm}^{-1}$, the structure of the ELRC also has a complex "double-spike" character. 3) The main peaks and the minimum in the reflection are shifted toward longer wavelengths, respectively, by ~ 8 and $4\ \mathrm{cm}^{-1}$ relative to the positions which they should occupy in the spectrum of the crystal without SCL. This peculiarity is clearly evident in Fig. 2b, which shows the theoretical reflection spectra. We also note that the nonvanishing reflection in the main minimum amounts to several percent.

To explain the form of such ELRC it is necessary to invoke a complex model of the surface potential of the exciton (see Fig. 2a). The sharp drop of the resonance

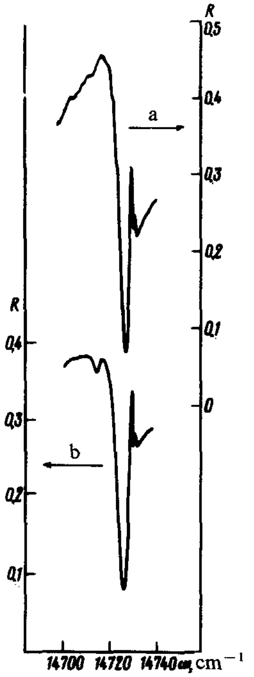

FIG. 1. Experimental dependences of the coefficient of reflection on the frequency for a CdSe crystal. $T = 4.2$ K. $E \perp C$. a) Starting state, b) after irradiation by 3-keV electrons.

frequency ω_0 near the surface is apparently related to the fluctuation part of the electric field of charged defects (donors) with very high concentration ($\gtrsim 10^{18}$ cm^{-3}), which, on the one hand, acts on the excitons as an additional field (the exciton does not feel the sign of the fluctuation) and, on the other, accounts for the bound states at the centers (of the type I_3). For an effective field which deforms the surface well and for the corresponding damping Γ, we chose the value 5.6×10^3 V/cm, which is much lower than the critical field required for the existence of an exciton: 3×10^4 V/cm. The potential also has an extended "tail" in the region farther from the surface. In this extended region the position of the Fermi level is such (this is attributable to the presence of a depletion field) that the donors are neutral; the corresponding flat section of the potential is formed due to finer charged impurities with low concentration $\sim 10^{14}$ cm^{-3}.

The method for calculating ELRC for a given potential is described in Ref. 1. This method permits circumventing the difficult problem of finding the levels of mechanical excitons in the well and then taking into account the interaction between the light and the exciton, and it makes it possible to calculate directly the optical spectra of excitons. As is evident from Fig. 2b, all of the peculiarities of the observed spectra listed above are reproduced well. By varying the parameters we arrive at the following conclusions. The shift of the basic characteristics of the spectrum toward longer wavelengths is related to the overall position of the resonance frequency of the exciton at the surface. Inclusion of the damping Γ also leads to an additional shift. The oscilla-

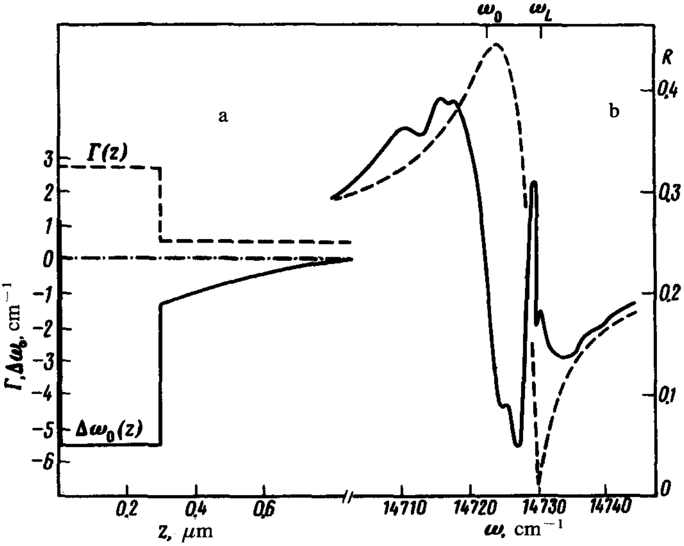

FIG. 2. a) Dependences of the shift in the resonance frequency of the exciton and damping Γ on the distance from the surface z, used in calculating the ELRC. b) ELRC of CdSe calculated using the method of Ref. 1 for the parameters used in Ref. 7 (solid curve). The dashed curve shows the unperturbed ELRC (i.e., that which occurs in the absence of a surface potential).

tions at the reflection peak and the "double-spike" structure are related to the quantized states of the exciton in the well. The shape of the spike structure is determined by the shape of the "tail" of the exciton potential. Three or more spikes can be obtained by increasing the length of the tail. The energies of the states of the mechanical exciton in the well, we might note, do not necessarily coincide with the spectral features corresponding to them (which is characteristic for atomic spectroscopy). The correspondence rule for a simple infinite square well is given in Ref. 5.

The results presented above show that the complex structural reflection spectra observed experimentally can be explained by an appropriate choice of the surface potential. This cannot be done within the framework of the old theories, which make use of the variation of the additional boundary conditions and the thickness of the dead layer in the manner suggested by Hopfield and Thomas.[6] The study of complex ELRC opens up new possibilities for studying the surface region of semiconductors, and the fact that this is a contact-free method of investigation is an important asset.

1)Our studies have shown that it is sufficient to take into account only the mean field in order to explain a number of ELRC. A detailed analysis of this problem will be reported in another paper.

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