Shaping of the exciton optical reflection spectra of CdSe crystals bombarded by low-energy electrons

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(Submitted 31 March 1995)
Pis'ma Zh. Éksp. Teor. Fiz. **61**, No. 10, 791–795 (25 May 1995)

The evolution of the spectra of exciton optical reflection of CdSe crystals at $T=4.2$ K during bombardment of the samples with "slow" (2-keV) electrons has been studied in detail. The mechanism which shapes the surface exciton potential has been identified. It involves a universal electron energy-loss function. © *1995 American Institute of Physics.*

The surface region of a semiconductor strongly influences exciton optical spectra because of the pronounced perturbation of exciton states near the surface.[1] These perturbations are caused by the purely spatial limitation imposed on the motion of an electron–hole pair by the surface and also by the constantly occurring variations in the physical properties of the material over a certain distance from the surface. As a result, a distinctive exciton surface transition layer arises. The properties of this layer can be studied effectively by exciton spectroscopy, in particular, by optical reflection spectroscopy. By applying various agents to the surface of a semiconductor, one can alter the characteristics of the transition layer and thus the exciton optical spectra. The spectra can be utilized as a sensitive instrument for studying the mechanisms shaping the surface transition layer.

In this letter we are reporting some careful measurements of exciton specular-reflection spectra of CdSe crystals subjected to electron bombardment in various doses. We observe some clearly expressed changes in the spectra as a result of the bombardment. Analysis of these changes reveals a direct relationship between the structure of the surface transition layer which forms and a universal electron energy-loss function in a condensed medium.[2]

The measurements were carried out at a sample temperature $T=4.2$ K in the spectral region of the $A_{n=1}$ exciton resonance with a light polarization $E\perp C$, where C is the hexagonal axis of the crystal. In the special cryostat which was used, the samples were bombarded with electrons at $T=4.2$ K just before *in situ* measurements of the reflection

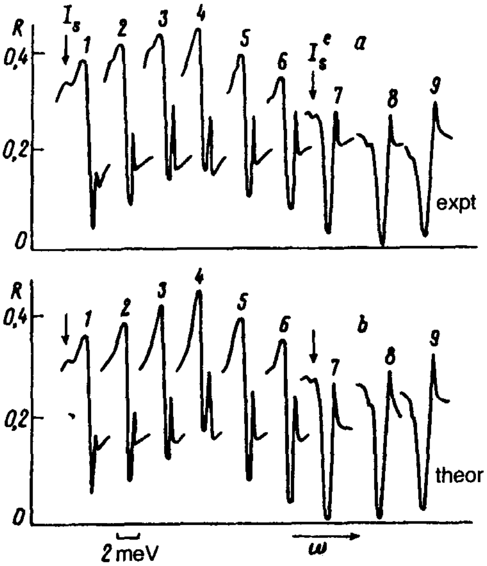

FIG. 1. Optical reflection spectra of a CdSe crystal in the region of the $A_{n=1}$ exciton state. a: Experimental spectra at $T=4.2$ K for the polarization $E\perp C$. *1*—Original spectrum; *2–9*—with increasing electron-bombardment dose (see the text proper). b: Theoretical spectra for various values of the field F_s (*1–4*) and of the damping parameter Γ_s[meV] (*5–9*) at a semiconductor surface. *1*—0.08; *2*—0.15; *3*—0.20; *4*—0.24; *5*—0.09; *6*—0.18; *7*—0.66; *8*—1.5; *9*—3.0. For curves *8* and *9*, the values of the imaginary part of ϵ_b are nonzero, specifically, 0.7 and 1.4, respectively.

spectrum. Curves *1–9* in Fig. 1a show experimental reflection spectra of CdSe samples subjected to an increasing dose (as reflected by the curve number) of electrons with an energy $E=2$ keV in a flux density of 7×10^{15} $e^-/(\mathrm{cm}^2\cdot\mathrm{s})$. We see from this figure that the bombardment causes fundamental quantitative and qualitative changes in the spectra.

In the first stage of the bombardment (*1*—0 s, *2*—5 s, *3*— 20 s; *4*—65 s) we observe a significant increase in the reflection coefficient R in the spectral region of the main minimum, accompanied by an intensification of a sharp spike-shaped feature near this minimum. The symmetry of this spike, as determined from the ratio of the minima of R near the spike, is changed primarily by an upward motion of its long-wave base. At the same time, in stage *1–4*, there is an increase in R at the main maximum, while the structural feature I_s, in the form of a small maximum on its long-wave wing, gradually disappears.

In the next stage of the bombardment (*5*—135 s, *6*—225 s, *7*—405 s), there is a significant decrease in R, both near the main maximum and at the main minimum of the reflection. The spike becomes much more asymmetric, because of a significant downward motion of its long-wave base, while the value of R at the crest of the spike remains essentially constant. There is a transformation of the spectrum from a dispersive shape to an antidispersive shape (a "rotation" of the reflection spectral line). Another structural feature, I_s^e, arises on the long-wave wing of the spectrum, in the form of a local minimum, which is slightly on the short-wave side of the I_s maximum observed in the initial stage of the bombardment.

With a further increase in the bombardment dose (*8*—645 s, *9*—1245 s), the antidispersive shape of the reflection spectrum becomes progressively more prominent: The long-wave knee in the spectrum shrinks, the main minimum of R begins to grow progressively, and the value of R at the crest of the spike increases slightly. In all stages of the bombardment the spectral position of the spike observed at the frequency $\omega_L = 1.826\,08$ eV remains the same.

The electron bombardment of the crystal surface thus causes the exciton optical reflection spectra to undergo some nontrivial structural changes, which indicate substantial changes in the properties of the surface transition layer due to the electron bombardment.

The main qualitative features of the evolution of this transition layer due to electron bombardment were pointed out in Refs. 1 and 3–5. It was suggested that the changes caused in the properties of the surface transition layer in CdSe crystals during electron bombardment stem from the formation of radiation defects and the transformation and charge exchange of surface states (centers). There is thus the possibility that the transition layer formed by electron bombardment in CdSe crystals constitutes a region near the surface in which the defect composition and the charge state are quite different from those in the interior of the crystal (the surface region would be a "defective" layer and a space-charge layer).

It is natural to suggest that the mechanism for the perturbation of an exciton in a transition layer of this sort would involve the interaction of the exciton with the electric field of the space-charge layer and with centers in the surface defective layer. The interaction with the surface electric field causes a shift of the resonant frequency of an exciton, ω_0, through the Stark effect. It also leads to an increase in the dissipative damping of an exciton, Γ, along the direction toward the surface, because of an increase in the probability for a field-induced dissociation of the exciton with increasing field strength.[1] The effect of the defective layer on the exciton would consist of an increase in Γ for the exciton in this layer, as a result of scattering and a decrease in the exciton lifetime because of an effective binding of excitons at centers in the defective layer.

A surface transition layer formed by electron bombardment is thus described by a complex surface exciton potential whose real part is determined by the profile $\omega_0(z)$, and whose imaginary part is determined by the profile $\Gamma(z)$ (the z axis is directed into the interior of the crystal, along the normal to the plane of the surface). The specific form of the surface exciton potential created by the electron bombardment is thus determined by the distribution of the concentration of radiation defects and of the electric field near the surface. It is logical to suggest that the profile of the concentration of radiation defects reproduces the profile of the electron energy loss in the bombarded crystal. This dependence also determines the distribution of the electric field near the surface of CdSe subjected to electron bombardment, since intrinsic defects in CdSe crystals and other II–VI compounds act as electrically active shallow centers, which usually form a surface space-charge layer.[6,7] For low-energy electrons, the spatial distribution of their energy

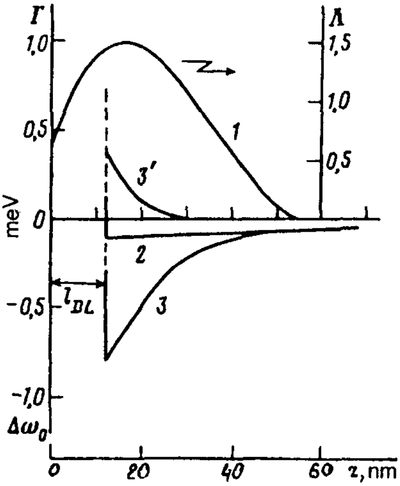

FIG. 2. *1*—Universal electron energy-loss function Λ for an electron energy $E=2$ keV; *2,3,3′*—shift of the resonant frequency, $\Delta\omega_0$ (*2, 3*), and the damping Γ (*3′*) of an $A_{n=1}$ exciton versus the coordinate z in the surface electric field. Curve *2* was calculated for the field determined by the parameter values $F_s=0.08$ and $N^+(z)=6\times10^{14}$ cm^{-3}; curves *3* and *3′* were calculated for the field set up by electron bombardment and determined by the parameter values $F_s=0.24$ and $N_s^+=3.8\times10^{15}$ cm^{-3}.

loss can be approximated by a universal function, specifically, a cubic polynomial of the coordinate divided by the electron range, y:

$$\Lambda(y)=0.6+6.21y-12,\ 4y^2+5.69y^3.$$

Here $y=z/w$; w is the effective electron range, found from the condition[8] $\rho(\mathrm{g/cm^3})w(\mathrm{cm})=10^{-5}E^{1.5}(\mathrm{keV})$; and ρ is the mass density of the material. Curve *1* in Fig. 2 is a plot of the function $\Lambda(x/w)$ for $E=2$ keV.

Using the function $\Lambda(y)$, we carried out some quantitative calculations of the exciton optical reflection spectra in the model of a multilayer medium in which the layers differed in the parameters of the excitons, in accordance with a step approximation of the actual exciton potential.2) The model also incorporates the surface "dead" (exciton-free) layer (DL) of intrinsic nature, with a thickness on the order of two exciton radii3) ($l_{\mathrm{DL}}=12$ nm) (Ref. 9).

According to the model adopted, the structure and transformation of the exciton optical reflection spectra in the initial state (before the electron bombardment) and in the initial stages of the electron bombardment (at doses $\lesssim 5\times10^{17}$ e^-/cm^2; curves *1–4* in Fig. 1) are determined by the surface exciton potential shaped by the electric field of the space-charge layer (curves *2*, *3*, and *3′* in Fig. 2). The space-charge layer is characterized in its initial state by a uniform distribution of the density of positive space charge $[N^+(Z)=6\times10^{14}\ \mathrm{cm}^{-3}]$. It forms the surface electron potential shown by curve 2 in Fig. 2. [For the selected scale along the Γ axis, the damping curve $\Gamma(z)$ corresponding to the initial field merges with the z axis, so it is not seen in this figure.]

The electron bombardment generates a profile of positive space charge against the background of the initial stepped profile $N^+(z)$. This new profile coincides with the electron energy-loss profile $\Lambda(y)$, leading to a corresponding modification of the surface transition layer.4) To illustrate the modification of this transition layer by the electron bombardment, curves *3* and *3'* in Fig. 2 show the surface exciton potential used in the calculation of reflection spectrum *4* in Fig. 1b.

In the following stages of the electron bombardment (at fluxes $\gtrsim 10^{18}\ e^-/\mathrm{cm}^2$), the parameters of the space-charge layer remain constant. In these stages of the bombardment (curves *5–9* in Fig. 1b), the reflection spectra evolve as a result of a change in the parameter $\Gamma(z)$, whose profile along the coordinate is also described by the function $\Lambda(y)$. The increase in Γ, which depends on the coordinate z, corresponds to the onset of a nonuniform defective layer, as a result of the prolonged effect of the electron bombardment.[3]

The adjustable parameters in the model which lead to the transformation of the *reflection spectra are the space-charge density* N_s^+ *and the dissipative exciton damping* Γ_s at the surface of the semiconductor.5) The values of these parameters were chosen by fitting the theoretical reflection spectra to the experimental spectra. Also working from the requirement of an agreement with experiment, we introduced an additional parameter in the calculation of the spectra corresponding to extremely high electron fluxes (curves *8* and *9* in Fig. 1b). This new parameter determines the imaginary part of the background dielectric constant ϵ_b. From the physical standpoint, the introduction of an imaginary increment in ϵ_b corresponds to the incorporation of a spreading of the fundamental absorption edge at high electron flux rates, as has been observed experimentally in thin CdSe samples after prolonged electron bombardment.

The structural features I_s and I_s^e seen in the experimental spectra are reproduced in the calculations by introducing some additional, oscillatory terms in the expression for the dielectric constant. This approach corresponds to incorporating in the model some effects observed experimentally: a binding of excitons by surface centers (or defects) [12] (I_s) and by near-surface centers[3] (I_s^e).

The good agreement observed between the experimental and theoretical spectra, the small number of parameters in the theory, and the physically justified assumptions underlying the model indicate that this model adequately reflects the actual physical picture. The method developed here for describing the surface transition layer formed by the electron bombardment demonstrates the power of exciton spectroscopy for studying the structure and properties of the surface regions of semiconductors.

This study was supported by the Center for Grants in Fundamental Natural Science of the State Committee on Higher Education of the Russian Federation (Grant 94-7.10-3112).

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2) Theoretical aspects of the model and of the method used to calculate the reflection spectra will be reported in a separate paper.

3) See Ref. 10 regarding the need to consider a layer of this sort in order to find a correct description of the surface transition layer.

4) In the initial stage of the electron bombardment of CdSe crystals, there may also be a decrease in the electric

field near the surface, because of an electron-stimulated desorption of electronegative gases from the surface.[11]

[5)] The field at the surface, $F_s = E_s / E_i$, where E_s is the field at the surface, and E_i is a critical field for ionization of excitons, could also be used as an adjustable parameter of the model. This parameter is functionally related to N_s^+.

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Translated by D. Parsons