Surface and volume emission of excitons in the luminescence spectra of CdS crystals

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A detailed study is made of evidence for the I_s band (486.3–486.5 nm) of CdS crystals in samples differing in the nature of the free-exciton kinetics. A relationship between I_s and a space charge layer is demonstrated. When free excitons are pulled into the space charge layer, their lifetime is affected.

There are usually space charge regions near the surfaces of semiconductors in which the electric field reaches high values. On the one hand, such fields can pull excitons into the surface regions,[1] and on the other they can give rise to states that are localized near surfaces—so-called mechanical surface excitons.[2] An I_s band has been observed[3,4] in the luminescence spectra of CdSe and CdS crystals in the region just below the exciton ground state (for brevity, we will call this region the "forespectrum"[5]). Because of its high sensitivity to bombardment by low-energy electrons, this band has been attributed to the emission of mechanical surface excitons. In the present experiments we studied the kinetic properties of the I_s band in CdS crystals.

We studied the luminescence spectra of a large number of samples (about 70) of CdS crystals at $T = 2$ K. We used both wafers and bulk crystals with various exciton lifetimes τ (τ was estimated from Ref. 6). We recorded spectra in the arrangements $\mathbf{k} \perp c$ and $\mathbf{E} \perp c$. The excitation intensity did not exceed $\sim 10^{19}$ photons/(cm^2·s).

In the region 486.3–486.5 nm we observe I_s bands in the luminescence forespectrum of essentially all of the samples, along with narrow lines corresponding to the luminescence of exciton-impurity complexes. Figure 1 shows some of the most representative spectra. The arrow marked E_L and E_T show the energies corresponding to the bottoms of the bands of longitudinal and transverse excitons. Also shown here are

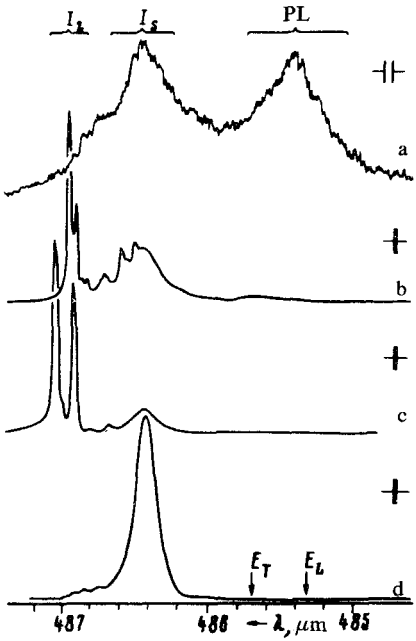

FIG. 1. Exciton luminescence of two bulk samples with different exciton lifetimes (a—$\tau \sim 5 \times 10^{-11}$ s; b—$\tau \sim 10^{-9}$ s) and of two high-quality wafer samples of different thicknesses (c—$d = 6$ μm; d—$d = 0.25$ μm).

the regions of the polariton luminescence (PL) of free excitons and the luminescence of excitons bound by neutral donors[7] (I_2). The positions and number of the I_2 lines and of the other narrow lines of exciton-impurity complexes vary from one sample to the next. In the bulk samples, with short lifetimes τ, the I_s band is the most intense component of the forespectrum, against a weak overall intensity; the I_2 line is essentially missing (Fig. 1a). With increasing τ and increasing overall intensity, the relative intensity of I_s decreases (Fig. 1b). In the thicker of the high-quality wafer samples (5–40 μm), the relative intensity of I_s is low (Fig. 1c). With decreasing thickness d of the wafers, the relative intensity I_s increases. In the thinnest samples, the I_s band is the most intense component of the forespectrum (Fig. 1d; see also Refs. 8 and 9).

It can be seen from Fig. 1 that in all cases a decrease in the I_2 intensity leads to an increase in the I_s intensity, and vice versa (the I_2 and I_s intensities are negatively correlated). This is a typical situation for the relative numbers of excitons bound by neutral and ionized donors.[7,9] This circumstance has stimulated the interpretation of I_s as due to exciton-impurity complexes at ionized donors in several studies. The primary objection to the identification of I_s as the emission of an ordinary (volume) exciton-impurity complex is the large half-width of the I_s band (2×10^{-2} nm): far larger than the half-widths of all the observed lines of exciton-impurity complexes, including the half-width ($\sim 2 \times 10^{-3}$ nm) of the I_s line (486.17 nm), whose interpretation as the emission of an exciton bound to an ionized donor has a solid basis.[7]

Analysis of the observed negative correlation between I_2 and I_s suggests that I_s has a surface origin and is associated with a space charge layer. In the samples with

short lifetimes τ, the excitons do not have time to change the spatial distribution that arises upon the absorption of light. The energy relaxation leads to a filling of states exclusively near the surface. The high relative intensity of I_s as a surface state would be quite natural in this case. The obvious absence of the I_2 line indicates that the emission comes from a depleted layer in the space charge region, where there are no neutral donors. In samples with large values of τ, the excitons diffuse substantial distances (5–7 μm; Ref. 10), reach regions where the donors are neutral, and are captured there, with the result that I_2 is the most intense component in the forespectrum. With decreasing d, the relative volume in which surface curvature has no effect decreases. As a result, the fraction of the emission represented by I_2 decreases in the thin samples; this fraction is proportional to the size of the region outside the space charge region. The fraction of the emission which is surface emission, I_s, increases.

As mentioned earlier, a surface field can pull excitons to the surface, so that it should affect the effective value of τ for free excitons.[1] We have found it possible to demonstrate a decrease in τ due to the capture of excitons to surface states corresponding to the I_s band. The decrease in τ is seen in the dependence of the relative intensities of the volume and surface components of the emission of high-quality wafer samples on the sample thickness in a spectral region separated from the resonance by the energy of two LO phonons. We measured the ratio (A) of the integral intensities of the PL-2LO bands to those of the I_s-2LO bands. These bands arise from the emission from the corresponding states accompanied by the simultaneous production of two LO phonons. In contrast with the resonance region, where the relative intensity of the polariton luminescence is strongly affected by the capture of polaritons,[11] the intensity of the PL-2LO band is proportional to the total number of excitons over the entire volume. Consequently, the ratio A is a measure of the ratio of the total number of free excitons to the number of excitons captured at the surface. Figure 2 shows that the relative number of excitons captured by surface states increases with decreasing d, so

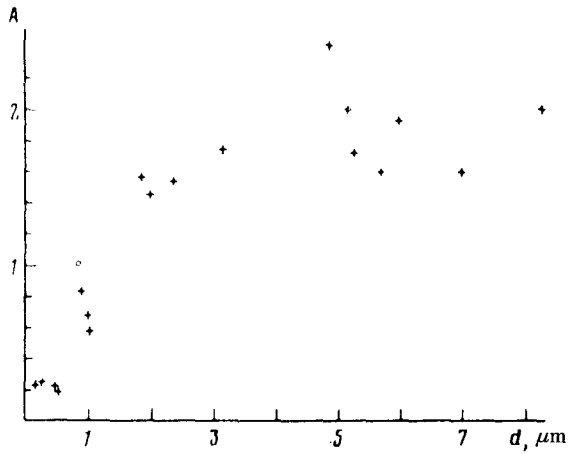

FIG. 2. The ratio (A) versus the thicknesses of wafer samples according to measurements from spectra obtained under identical excitation and measurement conditions.

that there is a decrease in the number of free excitons. The evident reason for this behavior is a shrinkage of the region in which the surface electric field of the space charge region is not a factor. This mechanism is apparently one reason for the observation in Ref. 10 of a decrease in τ for thin samples. The ratio begins to decrease at values $d \sim 1.5$–$2\ \mu$m. These values can be taken as an upper estimate of the thickness of the space charge region that arises in CdS wafers ($d_{SC} \sim d/2 \sim 0.7$–$1\ \mu$m).

What is the nature of I_s? As we have already mentioned, the negative correlation between I_2 and I_s is consistent with the behavior of I_s as resulting from an exciton bound by an ionized donor. If, however, we do identify I_s as resulting from an exciton at an ionized donor, then in view of the link with the surface demonstrated above, we should interpret I_s as a surface exciton-impurity complex in the space charge layer. In this case, the large half-width of I_s can be attributed to differences in the strengths of the electric fields acting on the level of the exciton-impurity complex at various points in the space charge region. Another possibility is to identify I_s with the emission of mechanical surface excitons.[2–4] At present, it is difficult to reach a definite conclusion regarding the nature of I_s. It is possible that excitations of both types are contributing to the observed emission.

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