Surface excitons with a hole localized in a quantum inversion layer

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A new structure has been discovered in the photoconductivity spectrum of CdS. The spectral position and intensity of this structure are extremely sensitive to the parameters of the space-charge layer, controlled by a special illumination. This structure is attributed to the excitation of quasi-2d surface excitons with a hole localized in a quantum inversion layer.

In this letter we report the observation of structure of a new type in the photocurrent spectrum of CdS crystals at 4.2 K. This structure can be caused by intense illumination of the crystals in the region ≤ 510 nm. In a dc measurement, the structure is a maximum which arises at 15–20 meV on the long-wave side of the $A_{n=1}$ exciton. This

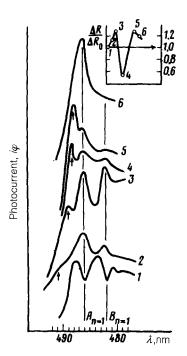


FIG. 1. Photocurrent spectra of a CdS crystal at 4.2 K after intense illumination for the following time intervals: 1—0; 2—2; 3—5; 4—10; 5—15; 6—20 min $(E \perp C)$. The additional peak is shown by the arrow. The inset shows the peak-to-peak amplitude of the reflection line, $\Delta R = R_{\text{max}} - R_{\text{min}}$, versus the illumination (the doses are the same, but their effects on the space-charge layer may not be exactly the same in reflection and photoconductivity experiments). Here ΔR_0 is the initial amplitude of the line.

maximum undergoes a marked shift in the long-wave direction with increasing illumination dose¹⁾ (Fig. 1). The intensity of this maximum increases significantly, and its half-width decreases, as it approaches the $A_{n=1}$ exciton. At long exposures, it becomes the predominant feature in the spectrum. Its limiting position is that of the $A_{n=1}$ exciton. The structure which is observed during ac measurements (300-600 Hz) is a series of maxima spaced at intervals $\sim 10^{-2}$ eV; these maxima also shift toward the position of a free excition with increasing illumination (Fig. 2). These features of the photocurrent spectrum are seen when the polarization of the light is that allowed for A exciton: $E \perp C$. A series of maxima analogous to that shown in Fig. 2 is observed in the $E \parallel C$ polarization. Its limiting position is the exciton $B_{n=1}$. It is natural to assume that the observed effect is a consequence of excitons which are localized near the surface. These excitons could not, however, be localized collectively in a surface well, since (in view of the small width of the maxima in the photocurrent spectrum) they would be manifested in the reflection as isolated structural features.^{1,2} No such features are seen in the reflection.

The inset in Fig. 1 shows the peak-to-peak amplitude, $\Delta R = R_{\text{max}} - R_{\text{min}}$, of the exciton reflection line for the $A_{n=1}$ exciton as a function of the illumination. The behavior is complicated and not monotonic. Analysis of the effect on this amplitude of

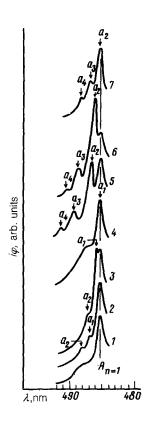


FIG. 2. Photocurrent spectra of a CdS crystal in its initial state and with increasing illumination dose. Fast component. T = 4.2 K; $E \perp C$.

the nonuniform field in the space-charge layer near the surface³ has shown that this behavior is caused by an increase (during doses 1-4) and a decrease (4-6) in the field E in the depletion layer (the solid lines in Fig. 3) and also by the attainment, at doses 3 and 5, of conditions close to the optimum conditions for a quasilocalization of a 3D exciton by a Stark well.^{4,3} The result is an intensification of the exciton reflection line.⁵ (In other words, localization of the excitons as a whole is observed, but as an independent phenomenon, which leads to a structureless intensification of the exciton reflection line).

At dose 4 the depletion layer has a space-charge density $\sim e \times 10^{17}$ cm⁻³, a maximum field $\sim 10^5$ V/cm, a thickness ~ 15 nm, and a band curvature $\sim 10^{-1}$ eV. Several 2D subbands, spaced at intervals $\sim 10^{-2}$ eV, split off from the valence bands here; i.e., there is the possibility of a localization of holes near the surface.

The most probable reason for the field increase in doses 1-4 is a charging of surface states.⁶ These states apparently also determine the long times required for relaxation to the original state: on the order of minutes. The surface charge is estimated to be $\sim e \times 10^{11}$ cm⁻². Dose 4 corresponds to saturation of the surface-state charge. The field decay that follows it would naturally be attributed to the formation of an inversion layer upon the filling of the deepest subbands by holes. The corresponding field is shown nominally by the dashed lines in Fig. 3. With increasing hole concentra-

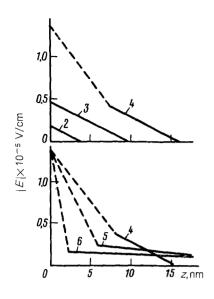


FIG. 3. Suggested coordinate dependence of the electric field, E(z), after a special preliminary illumination (the doses are the same as in Fig. 1).

tion (to $\sim 10^{11}$ cm⁻²), the subbands should be ejected from the channel. This circumstance combines with the order-of-magnitude agreement of the intervals between the subbands and those between the structural features in the photocurrent spectrum to provide evidence that the observed structure is related to optical transitions from 2D subbands. A question of fundamental importance here is that of the final state: Is an exciton produced, or is the hole that appears different in no way from those that already exist? The limiting position of the components of the structure and also the peak nature of the structure in the 2D problem are evidence for the first possibility. It is pertinent to note here that in the motion of the components of the structure in the photocurrent spectrum—a motion which is monotonic on the whole—there is an intermediate hold at resonance with the position of an exciton related to the charged donor I_3 . This circumstance is again understandable, since 3D excitons in the depletion layer are in the field of ionized donors.²⁾

We thus find quasi-2D excitons with a hole that is weakly bound by a quantum layer. The low oscillator strength of the transition is explained by the circumstance that the transition is determined by an overlap of the tails of the wave functions of an electron in the volume and of a hole in the channel. During the delocalization of a hole, the excitons become 3D excitons, with a corresponding increase in oscillator strength. The screening by the holes in the channel also becomes progressively less important and delocalization proceeds.

As we have already mentioned, the structure observed in the photocurrent spectrum is not seen in the reflection. Its presence in the photocurrent spectrum is attributed to the greater sensitivity of this method. Superficially similar effects have been seen in the luminescence of metal-insulator-semiconductor structures⁷ and semiconductor heterostructure.⁸

We wish to thank I. N. Ural'tsev for useful discussions.

¹⁾The absorption spectra of barrier structures show a band, in the same frequency range, which shifts 10–15 meV in the long-wave direction upon the application of a voltage of 10–100 V in the cutoff direction.

²The hold at 77 and 273 K occurs when the excitation energies of the surface exciton and of the exciton bound by a neutral acceptor (I₁) are equal.

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