Observation of excitons in thin surface layers of CdS

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Anomalies of the dispersion and the appearance of a new band in the spectrum of the reflection from the surface of a CdS single crystal bombarded with Ar^{40} have been observed, simultaneously with a sharp increase of the intensities (I_2) of the emission of the band of excitons bound on V_s and of the electron-hole condensate in the surface layer (P_s band).

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Interest in the studies of the properties of excitons in the surface region of II-VI crystals is due to the anomalies of the excitonic reflection spectra observed in a number of studies (see, e.g.,[1–4]). In all cases, the explanation of the results reduces to effects of spatial-dispersion[5] and to the existence of the so called "excitonless" region of the crystal near its surface.

Up to now, however, all these investigations were performed either on thick transition layers (hundreds of angstroms) or with uncontrolled action on the surface of the crystal.

We report here the first study of the properties of excitons in a thin (50 Å) surface region produced in CdS crystals either by cleavage or by low-energy ion bombardment.

We investigated the excitonic reflection spectra (Fig. 1) and photoluminescence (PL) spectra (Fig. 2), of CdS single crystals excited at $T=4.2$ K with ordinary light (DRSh-500 lamp) and with an LGI-21 nitrogen laser light. We used pure (1010) cleaved surfaces of single crystals obtained in liquid helium as well as in air. The crystal surfaces were bombarded with Ar^{40} ions (ion energy $\lesssim 1$ keV, dose D in the range from 2×10^{13} to 5×10^{15} ions/cm^2). In accordance with Lindhard's theory,[6] the depth of penetration of the ions did not exceed 50 Å, as confirmed by direct experiments on etching of the CdS surface. We note that the spread of the dispersion of the reflection in the case of cleaved surfaces obtained in liquid helium was much larger than for surfaces obtained in air.

It is seen from Fig. 1 that bombardment even at $D=2\times10^{13}$ ions/cm^2 decreases substantially the amplitudes of the peaks, changes of the shape of the reflection curves, and shifts their minima towards the shorter wavelengths. An increase of D to 5×10^{13}–10^{14} ions/cm^2 broadens the structure of the spectrum (Fig. 1, curves 3 and 4), decreasing its amplitude, and shifts the minima further towards shorter wavelengths, causing a gradual "inversion" of the spectrum. Starting with $D=5\times10^{14}$ ions/cm^2, the shape of the spectrum, first, returns to its initial form (Fig. 1, curve 5) and second, acquires a new reflection peak at the wavelength $\lambda=487.1$ nm (with $\sim$40% polarization); with further increase of D this peak becomes predominant in the spectrum (Fig. 1, curve 6).

Bombardment is also accompanied by a decrease in the band intensities $I_1(\lambda=488.8$ nm) and $I_3(\lambda=486.5$ nm) and a sharp increase in the intensity $I_2(\lambda=486.9$ nm) of the line due to the emission of the excitons bound on the V_s sulfur vacancies (Fig. 2, curves 1 and 2). When the PL of the illuminated CdS surface is laser-excited, the intensity of the M band (I_M) increases somewhat and the intensity of P band (I_P) increases strongly in comparison with the unexcited surface. It

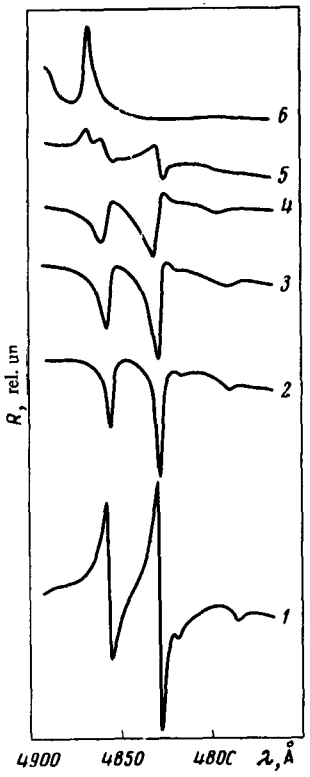

FIG. 1. Reflection spectra of a CdS surface cleaved in air (1) and subsequently subjected to ion-argon bombardment (2–6) at doses $D_1=2\times10^{13}$, $D_2=5\times10^{13}$, $D_3=10^{14}$, $D_4=5\times10^{14}$, and $D_5=5\times10^{15}$ ions/cm^2, respectively.

turned out in this case that I depends on the excitation energy like $I_{Ps}\sim L^{2.5-3}$, $I_{Ms}\sim L^2$, $I_{2s}\sim L^1$ (the subcript "s" labels here the bombarded surface).

Let us discuss the results. The absence from the reflection spectra of the fine structure (spikes) observed in[2] attests to a substantial increase of the damping ($\Gamma > 10^{-5}$ eV), or to strong growth of the thickness of the excitonless layer as a result of ion bombardment. Consequently, the "inversion" of the reflection spectrum at large irradiation doses can be attributed, in accord with[1,2] to broadening of the "excitonless" layer to a value ~ 200 Å, i.e., to a depth greatly exceeding the region into which the Ar^{40} ions penetrate. The onset of an excitonless layer of similar thickness for free excitons is, in our opinion, the consequence of their stronger binding to the surface defects ("drawing out" to the surface). The latter corresponds to an increase in the intensity I_2 after irradiation, Fig. 2. According to[7], the oscillator strength f_i for a bound exciton can exceed by several orders of magnitude the oscillator strength f_{ex} for the free exciton:

$$f_i = 8\left(\frac{\mu}{m}\frac{E_{ex}}{E_i}\right)^{3/2}\frac{\pi a_{ex}}{V} f_{ex},$$

where E_{ex} and E_i are the binding energies of the free and bound excitons, m, μ, and a_{ex} are the exciton mass, the reduced mass, and the Bohr radius of the exciton, respectively, and V is the volume of the unit cell.

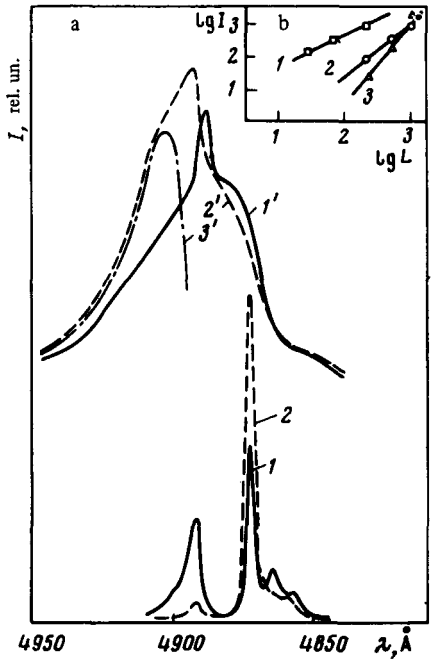

FIG. 2. Photoluminescence spectra of CdS crystals: 1,2—before and after bombardment when excited with a mercury lamp, 1′,2′—the same after excitation by focused laser beams, 3′—resolved P-band after bombardment.

On the basis of the data of Fig. 2, the values of E_{ex} and E_i remain practically unchanged by the bombardment, and μ in the surface layer usually exceeds somewhat the volume value,[8] and on the whole f_i is larger on the surface than in the volume.

It should be noted that localization of the excitons near the surface can be facilitated by virtue of the action of another mechanism—metallization of the surface. Indeed, bombardment of CdS by Ar^{40} ions leads to enrichment of the surface layer by Cd atoms which, at maximum D, as shown by microscopic investigations, form an island structure in the surface layer. The formation of such a layered (metal—semiconductor) structure leads, as a result of the action of the image forces,[9] to attraction of the excitons towards the interface of the structure and to the formation of a special branch of localized surface excitons that manifest themselves as a new band in the reflection spectra. In contrast to[3] this band appears at longer wavelengths than that of the free volume excitons, i.e., its appearance is not connected with a change in the frequency of the volume excitons near the surface.

Another typical fact is that the localization of the excitons at the surface leads to a sharp increase of the intensity of a rather broad P band, Fig. 2. Just as in the case of GaAs,[10] this circumstance points to the possibility of the formation of a surface electron-hole condensate in CdS at noticeably lower light intensities (on acccount of the stratification effect[11]) in comparison with the crystal volume.[12] Estimates yield for the surface-condensate line an energy position $E \approx 2.528$ eV, and a half-width $H \approx 10$ meV.

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