PIEZOSPECTROSCOPIC STUDY OF II-VI COMPOUNDS
WITH A STRUCTURAL TRANSITION OF THE
SPHALERITE–WURTZITE TYPE

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The results of studies of the piezospectroscopic effect for II-VI semiconductor compounds having a tendency

toward polymorphism and polytypy are given and the deformation potentials of materials with different
composition and structure are analyzed. The results obtained allow one to calculate the stress for II-VI
heteroepitaxial structures.

In creating optoelectronic structures based on multilayer heterostructures with quantum size effects, substantial
mechanical stress arises at heterojunctions due to the mismatched lattice parameters and the worsened quality of the structures. The stresses arising in heterojunctions in II-VI compounds are especially significant because their band structure details make them very promising materials for optoelectronics [1].

Substantially improved heterostructure parameters are possible using semiconductor solid solutions (SSS) which allow one on the one hand to achieve good matching of the lattice parameters, and on the other hand to provide quite high barriers for heterojunctions due to the strong dependence of the forbidden band width on the composition [1].

A number of zinc-containing II-VI SSS have a tendency toward polymorphism and polytypy which leads to a need to consider the possible structural transitions/junctions during the formation of heterostructures and corresponding analysis of the deformation effects [2, 3].

Since precise matching of the lattice constants at heterojunctions is impossible even using SSS, there is a need to determine the deformation potentials of various solid solutions, their concentration dependences, and changes due to structural effects, which will allow one to calculate the parameters of the heterojunctions.

The aim of this work is a piezospectroscopic study of Zn$_x$Cd$_{1-x}$Se solid solutions of different crystalline modifications and analysis of the concentration dependences of the deformation potentials for bulk single crystals and an analysis of the dependence of the deformation potentials of Zn$_x$Cd$_{1-x}$Se and ZnS on the crystal structure.

The Zn$_x$Cd$_{1-x}$Se and ZnS crystals for piezospectroscopic studies were prepared in the form of parallelopipeds with maximum dimensions 2 × 2 × 4 mm whose long sides coincided with the <111> axis of cubic and <0001> axis of hexagonal structures. The faces of the crystals are natural cleavage faces ([001] and [1120] planes respectively), and it was necessary to treat the faces with a polishing etch. Uniaxial compression was done in a special low-temperature press which provided highly uniform loading. The loading uniformity was monitored by recording the spectra from the four faces successively in a single loading cycle.

The piezoreflective exciton spectra were detected in polarized light of π(E || P) and σ(E ⊥ P) polarizations with nearly normal light incidence (the angle of incidence did not exceed 2°) and compressive stress from 0 to 25 kg/mm$^2$. We used a DFS-12 spectrometer or a ISP-28 spectrograph to record the spectra.

In the exciton piezoreflection spectra of the cubic crystals we observed splitting of an unpolarized line ($\Gamma_0-\Gamma'_0$ line) into two polarized components. In the spectra of anisotropic crystals a shift of the polarized components ($\Gamma_0-\Gamma'_0$, and $\Gamma'_1-\Gamma'_1$ transitions) are observed under deformation. The splitting and shift of the exciton levels is connected with splitting and shift.
Piezospectroscopic effects for excitons in II-VI crystals with the sphalerite (ZB) and wurtzite (W) structures which also have variable anisotropy (crystals with stacking faults) can be described by a general model [3-5].

During application of a uniaxial stress $P_{II} < 111>$ to a crystal with the ZB structure the crystal symmetry drops from $T_d$ to $C_{3v}$ and there is splitting of the basic eightfold degenerate (with account of the exchange interaction) state into two levels [3, 5]:

$$E_{1.3,5,7} = \frac{d'}{2\sqrt{3}} S_{14} P + E'_{14} (S_{11} + 2S_{12}) P,$$

$$E_{2.4,6,8} = \frac{d'}{2\sqrt{3}} S_{14} P + E'_{14} (S_{11} + 2S_{12}) P.$$  \(1\)

In anisotropic crystals the positions of the exciton lines which correspond to $\Gamma_2 - \Gamma_7$ and $\Gamma_1 - \Gamma_7$ transitions as a function of the deformation is described by [4, 5]:

$$E_{1.3,5,7} = \frac{d' \cdot \epsilon'_z \cdot \epsilon'_x}{V^3} + \frac{\Delta \epsilon}{3} + E'_{14} S_{1x} \epsilon_x,'$$

$$E_{2.4,6,8} = \frac{-d' \cdot \epsilon'_z \cdot \epsilon'_x}{V^3} + \frac{\Delta \epsilon}{3} + E'_{14} S_{1x} \epsilon_x,'.$$  \(2\)

In Eqs. (1) and (2) we have used the following notation: $E_{1.2.3...7.8}$ are the positions of the exciton levels, $d'$ and $E'_{14}$ are the deformation potentials for an exciton, $S_{1x}$ are the elastic constants for the material of interest, $\epsilon'_z = (S_{33} - S_{11})P$; $S_{1x} = (S_{33} + 2S_{13})P$; and $\Delta \epsilon$ is the splitting of the valence band due to the anisotropic crystal field.

The elastic constants $S_{1x}$ for ZnS needed for determination of the deformation potentials $d'$ and $E'_{14}$ of the excitons have been taken from [6] while for the Zn$_x$Cd$_{1-x}$Se solid solution they are not known. Therefore we have made corresponding estimates based on the known values of $S_{1x}$ for binary alloys of ZnSe and CdSe [6].

Here we have assumed that the quantities $\epsilon'_z$ and $S_{1x}$ vary with concentration $x$ of the solid solution by a linear law.

The results of piezospectroscopic studies of the Zn$_x$Cd$_{1-x}$Se SSS with concentrations $x = 0.90$ (curve 1), $x = 0.74$ (curve 2), $x = 0.57$ (curve 3), $x = 0.45$ (curve 4), $x = 0.031$ (curve 5), and $x = 0.22$ (curve 6), and the theoretical dependences calculated from Eqs. (1) (curves 1 and 2) and formulas (2) (curves 3-6) are shown in Fig. 1 respectively by points and solid lines. As the position of the exciton level we took the position of the inflection point of the dispersion curve for the normal reflection line of the exciton measured in eV. The investigation was done at 77 K; the samples were compressed along the $<111>$ direction for cubic crystals (1, 2) and along $<0001>$ for the anisotropic ones (3-6).

The concentration dependences of the deformation potentials found from calculations using Eqs. (1) and (2) are given in Fig. 2 by points such that the value of $d'$ is shown by dots and $E'_{14}$ by triangles. In this figure the dashed lines show the