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Cathodoluminescence in Doped CdP_2 and $CdSiP_2$ Crystals

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Some general features of the behaviour of Cu, Zn, Bi, and Mn impurities in $CdSiP_2$ and CdP_2 crystals are studied by analyzing electron beam-excited luminescence spectra measured in a temperature range of 6 to 300 K, as well as by determining their electrical parameters. The impurities are established to substitute mainly the cadmium in the crystalline lattice and to promote the formation of complexes of defects, which are radiative recombination centers. Cadmium vacancies as well participate in the defect complex formation processes. A radiation ascribed to interstitial cadmium-type defects, is discovered in $CdSiP_2$ crystals.

Исследованы некоторые общие закономерности поведения примесей Cu, Zn, Bi, Mn в кристаллах CdP_2 и $CdSiP_2$. Для этого проанализированы их спектры люминесценции при возбуждении электронным пучком, измеренные в температурном интервале 6 до 300 K, а также определены их электрические параметры. Обсуждается вопрос о роли примесей в формировании центров излучательной рекомбинации. Установлено, что эти примеси замещают преимущественно кадмий в кристаллической решетке и способствуют образованию комплексов дефектов, являющихся центрами излучательной рекомбинации. В процессах дефектообразования комплексов принимают участие также вакансии кадмия. В кристаллах $CdSiP_2$ обнаружено излучение, которое связывается с дефектами типа междоузельный кадмий.

1. Introduction

Studying radiative recombination processes on specially undoped CdP_2 [1] and $CdSiP_2$ [2] crystals discloses many common features in the structure of radiation spectra. In particular, structural bands due to excitonic transitions with the participation of nitrogen impurities are observed in the edge region in both cases. The nature of radiation bands in the long-wavelength region was studied with the use of crystals heat-treated in vacuum or in the vapours of components. This made it possible to ascertain that intrinsic lattice defects are responsible for the majority of bands.

It is very useful to compare the behaviour of dopants in these compounds and to study their effect on the formation of radiative recombination centres. II–IV–V_2 compounds are isoelectronic analogs of II–V_2 ones and have approximately the same values of the forbidden band width [3]. Due to this, some common regularities of the defect formation and hence also a similar nature of the long-wave radiation should be expected.

2. Experimental

Crystals grown by the method of sublimation (p-CdP_2) and of chemical gas-transport reactions (n-$CdSiP_2$) were used for the investigations. The crystals were doped in the course of their growth. Dopants were selected so that they are donors, acceptors, or iso-

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valent with respect to components of the compounds; the relations between tetrahedral ionic radii of the impurity and host elements being substituted [4] were taken into account.

The experimental conditions were the same as in [1]. Cathodoluminescence spectra were measured in the region of (1.1 to 2.3) eV in the range from (6 to 300) K. This made it possible to extract information on the conductivity type and carrier concentration [5, 6]. The impurity concentration was determined by the mass spectroscopy of secondary ions [7].

3. Results and Discussion

The following intrinsic defect types are possible in specially undoped crystals:

— cadmium (V_{Cd}) and phosphorus (V_P) vacancies, for $CdSiP_2$, defects V_{Si} may exist additionally;

— interstitial cadmium (Cd_i), silicon (Si_i), and phosphorus (P_i) atoms;

— complexes of defects, consisting of an interstitial atom and a vacancy for metal and metalloid sublattices.

Formation of antistructural defects is unlikely because of a considerable difference of tetrahedral radii and electronegativities of the constituent elements [4]. Also, formation of defect associations which can be an aggregation of several simple defects is quite possible. It should be taken into account that defects V_{Cd} for the compounds under investigations are acceptors and defects V_P are donors [5, 6].

Fig. 1 shows cathodoluminescence spectra of initial and doped CdP_2 (curve 1) and $CdSiP_2$ (curve 2) samples, recorded at 6 K. Some characteristic parameters of the crystals are given in Table 1. Let us analyze the effect of impurities on the cathodoluminescence spectrum.

The spectrum of CdP_2:Cu crystals, in contrast to that for the initial samples, exhibits an edge luminescence in the form of three "nitrogen" bands and a broad band with a radiation maximum at 2.01 eV. Spectra of $CdSiP_2$:Cu feature two structureless bands with maxima at 1.42 and 2.20 eV. Studies of the temperature quenching and kinetics of the afterglow of these bands did not allow to relate them to the participation of donor–acceptor pairs in the radiative recombination. The presence of "nitrogen" bands in the edge region rules out the assumption of formation of Cu_P defects. The disappearance of the fine structure in this spectral region for $CdSiP_2$ indicates an increase in the imperfection of samples.

Table 1

compound	dopant	N_D (cm^{-3})	n, p (cm^{-3})	$h\nu_{max}$ (eV)
CdP_2	Cu	1.5×10^{17}	$p, 3 \times 10^{15}$	2.01
	Zn	1×10^{18}	$p, 2 \times 10^{15}$	1.86
	Zn	2×10^{18}	$p, 6 \times 10^{12}$	2.08
	Bi	5×10^{16}	$n, 5 \times 10^{12}$	1.86; 1.29
	Mn	3×10^{18}	$n, 5 \times 10^{11}$	2.04
$CdSiP_2$	Cu	3×10^{17}	$p, 3 \times 10^{12}$	1.42; 2.20
	Zn	1×10^{18}	$n, 7 \times 10^{12}$	2.08; 1.15 to 1.40
	Zn	2×10^{18}	$n, 4 \times 10^{13}$	1.8 to 2.0; 1.93
	Bi	1×10^{17}	$n, 5 \times 10^{13}$	1.80 to 2.01
	Mn	2×10^{18}	$n, 2 \times 10^{13}$	1.9 to 2.3; 1.57; 1.25

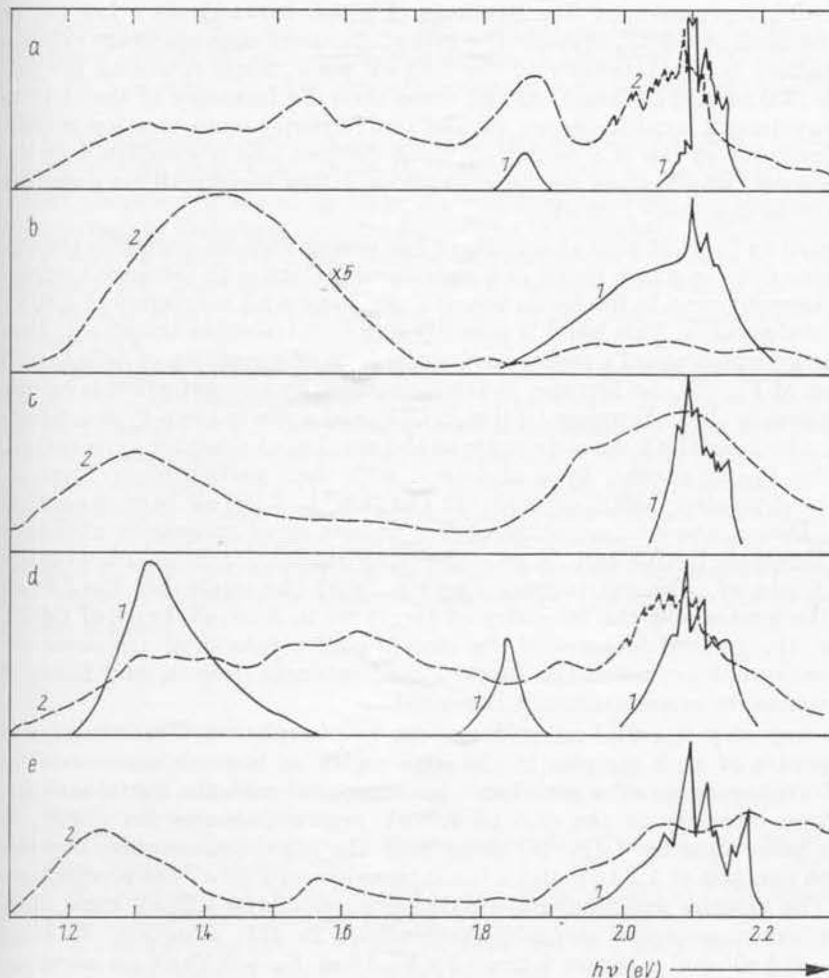

Fig. 1. Cathodoluminescence spectra of (1) CdP_2 and (2) $CdSiP_2$ crystals measured at 6 K. a) initial, b) Cu-, c) Zn-, d) Bi-, and e) Mn-doped

Copper with respect to cadmium is an acceptor. This is confirmed by an increasing concentration of acceptor-type centres both for CdP_2 (incresae in the hole conductivity) and for $CdSiP_2$ (right up to a conductivity inversion to p-type). For CdP_2 [7] at doping with copper its atoms preferentially substitute cadmium. The same phenomenon occurs also in $CdSiP_2$. However, this substitution process is accompanied by the formation of defect complexes, which are luminescence centres responsible for the appearance of new bands. At any rate, there are no reasons for relating them directly to the copper impurity.

Zinc is an isovalent impurity with respect to cadmium. Formation of substitutional defects Zn_{Cd} will be most probable in this case. The addition of zinc in the order of 1×10^{18} cm^{-3} to CdP_2 results in smearing out of the fine structure of the spectrum and appearance of a radiation band with maximum at 1.86 eV. A twofold increase in the zinc concentration leads to the disappearance of the band and an increase in the

edge radiation with a pronounced fine structure (Fig. 1c, curve 1). At a low (up to 10^{18} cm^{-3}) doping level of $CdSiP_2$ crystals the cathodoluminescence spectrum exhibits a substantial decline in the intensity of the 2.08 eV peak, while retaining the fine structure of the (2.0 to 2.2) eV band. At the same time the intensity of the (1.15 to 1.30) eV long-wavelength band increases. As the zinc impurity concentration is twice increased, the intensity of the (1.8 to 2.0) eV band declines and it overlaps with the edge of the spectrum, which gives rise to a single radiation band with maximum at 2.08 eV and an inflection near 1.93 eV.

It was suggested in [8] that zinc at relatively low concentrations promotes the formation of intrinsic defects which result in a considerable decline in the edge luminescence radiation intensity and in the formation of a new band with maximum at 1.86 eV in the CdP_2 crystal spectra. This band is possibly due to intracentre transitions from an excited to the ground state of a centre having the form of a complex of defects with the participation of V_{Cd} [9]. An increase in the zinc impurity concentration is accompanied by a decrease in the hole concentration in CdP_2 and a rise in the n-type conductivity of $CdSiP_2$, which results from a decrease in the number of acceptor-type centres. The latter can be V_{Cd} or another type of defects with their participation. From investigations of heat-treated $CdSiP_2$ crystals [2], the (1.80 to 2.00) eV band is ascribed to V_{Cd} defects. Hence, the concentration of V_{Cd} defects or of complexes of defects based on them increases in this case. A growth of the dopant concentration provides for an efficient filling of cadmium vacancies by zinc, with the result that the 1.86 eV band of CdP_2 disappears and the intensity of the (1.80 to 2.00) eV band of $CdSiP_2$ decreases. Thus, the general features of the zinc impurity behaviour are observed: at low concentrations it promotes the formation of intrinsic defects, and filling of defects V_{Cd} occurs as its concentration is increased.

The bismuth impurity is isovalent with respect to phosphorus. The structure of luminescence spectra of such samples in the edge region at bismuth concentrations up to 10^{16} cm^{-3} undergoes no substantial changes compared with the initial samples; only the radiation intensity in the (1.8 to 2.0) eV region decreases for $CdSiP_2$:Bi crystals. At the same time for CdP_2:Bi, along with the edge luminescence, luminescence bands with maxima at 1.29 eV and a less intense one at 1.86 eV are predominating. Studies of the kinetics and temperature dependences of the 1.29 eV band [3, 8] indicate that a donor–acceptor recombination occurs in this situation, Bi being a donor at $E_c - 0.5$ eV and a centre formed by $V''_{Cd}D^{\cdot}$ at $E_v + 0.27$ eV an acceptor.

Formation of Bi_P defects is unlikely because of a considerable difference in the tetrahedral radii [4]. Intrusion of Bi into Cd sites, i.e., formation of Bi_{Cd} defects, will be more preferable. With such an intrusion mechanism, bismuth behaves as a donor in both compounds. Investigating the electric properties of the crystals supports this suggestion: an increase in the n-type conductivity right up to inversion ($p \rightarrow n$) is observed in CdP_2:Bi, which is not characteristic of isovalent impurities.

Mn is a donor impurity with respect to all the components. In $CdSiP_2$:Mn, in contrast to CdP_2:Mn, apart from the egde radiation two radiation bands with maxima at 1.25 and 1.57 eV, respectively, as well as a broad luminescence band in the (1.9 to 2.3) eV region are observed, the band being formed by the superposition of several bands. The investigation of electron paramagnetic resonance spectra of Mn^{2+} in both compounds [10] demonstrates that ions Mn^{2+} isomorphously substitute cadmium. This agrees with the absence of (1.8 to 2.0) eV and 1.86 eV bands resulting from V_{Cd} defects. The luminescence of $CdSiP_2$:Mn crystals in the energy range of (1.9 to 2.3) eV appears to be due to intrashell transitions with the participation of the manganese d-shell in the course of its completion. The absence of some radiation bands is probably due to a high doping level (of the order of 3×10^{18} cm^{-3}), resulting in their broadening

and overlapping. Spectra of CdP_2:Mn crystals additionally include a band with a maximum at 2.04 eV, whose origin is similar to that of the 2.01 eV band in spectra of CdP_2:Cu, i.e., it is related to recombination on complex centres including a manganese impurity.

The following fact attracts attention to the spectra of $CdSiP_2$: for crystals containing Zn, Bi, Mn impurities, the cathodoluminescence in the energy region of (1.14 to 1.4) eV increases. Proceeding from the relations between the tetrahedral ionic radii, substitution of cadmium sites by impurities is probable. This favours the formation of Cd_i defects which are donor centres. Assuming the radiation to stem from "donor–valence band" transitions, we find that Cd_i defects give rise to an energy level $E_c -$ − (0.88 to 0.93) eV, which is also confirmed by the photoconductivity spectra of these crystals [11].

Luminescence with maxima at 2.01, 1.86, 1.29, and 2.04 eV arises in the spectra of Cu-, Zn-, Bi-, and Mn-doped CdP_2 crystals, respectively. It is most likely associated with the participation of V_{Cd} defects or of complexes based on them and including the dopants in recombination transitions. Formation of Cd_i-type defects occurs in the case of a heat treatment of CdP_2 crystals in saturated cadmium vapour. This results in the appearance of the 1.72 eV band in the luminescence spectra [1]. However, in contrast to $CdSiP_2$, this band has not been detected in all cases of doping. This can be ascribed to different atom packing densities in the compounds under investigation [12]. Since in cadmium diphosphide it is higher, the probability of formation of Cd_i defects is lower.

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