TRANSITION METAL IMPURITIES AND ELECTRONIC STRUCTURE OF ZnSe-BASED ISOVALENT SEMICONDUCTOR ALLOYS

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Energy level positions of the nickel 2+/1+ and cobalt 2+/3+ charge states have been used to estimate band edges for the valence and conduction bands of ZnSe-based alloys with cation (ZnCdSe) and anion (ZnSSe) substitution. Chemical trends in band offsets of heterostructures of Zn- or Mn-based II–VI compounds are analysed. Further on, the change of $Ni^{2+}(3d^8)$ and $Co^{2+}(3d^7)$ intra-d shell transition bands upon the alloying of host material is discussed.

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Properties of transition metal impurities in binary semiconducting compounds have been intensively studied and are, in the most cases, well understood. It has been demonstrated that $3d$ transition metal impurities are perfect "probes" for the study of compositional dependence of some fundamental characteristics of the electronic structure of semiconducting alloys, in particular, the respective band offsets [1–4] and of structural and compositional disordering. In our previous works [5–7] we undertook optical study of ZnMnSe, ZnCdSe and ZnSSe alloys doped with $3d$ transition metal ions to determine the energy level positions of the nickel 2+/1+ and cobalt 2+/3+ charge states through the wide composition range of the alloys. We derived respective band offsets as the energy difference of photoionization transitions. In this report we present new experimental data and discuss chemical trends in band offsets and behaviour of intra-d shell transition bands upon the alloying.

The single crystals $Zn_{1-x}Cd_xSe$:Co and ZnS_xSe_{1-x}:Co were grown by chemical transport method and doped with Co to the level 10^{18} cm^{-3}, approximately. Content of Cd ($x = 0 \div 0.5$) and S ($x = 0 \div 1.0$) was controlled by EDXRF
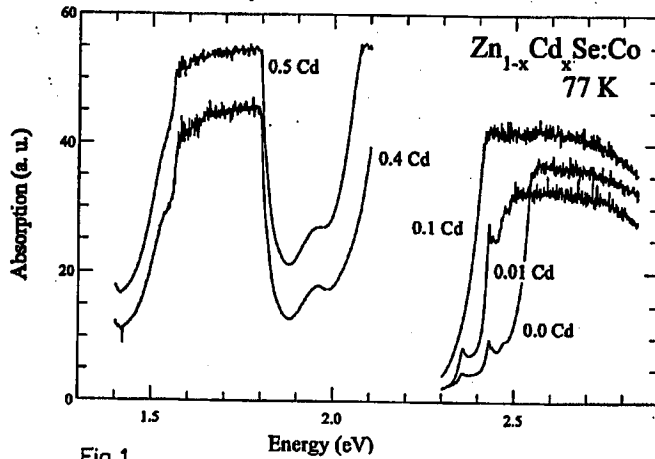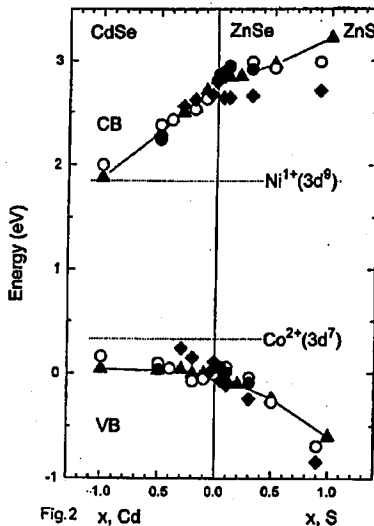
Fig. 1

Fig.2
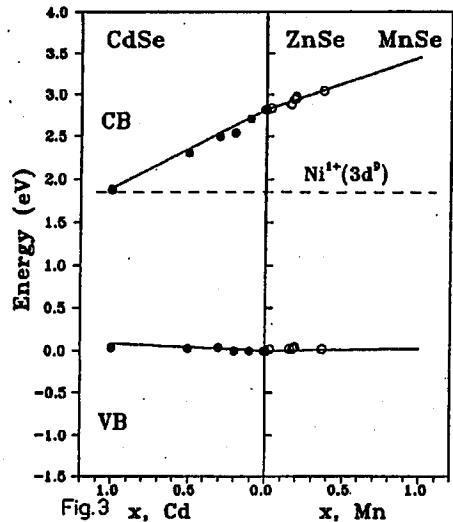

Fig.3

Fig. 1. Absorption spectra of $Zn_{1-x}Cd_xSe:Co$ near the photoionization threshold of the $Co^{2+} \rightarrow Co^{3+}$ and intra-shell $^4A_2(F) \rightarrow {}^4T_1(P)$ transitions for different alloy composition at $T = 77$ K. Details of the absorption spectrum between 1.5–1.8 eV and 2.5–2.9 eV could not be resolved due to too strong absorption.

Fig. 2. Valence band offsets of $Zn_{1-x}Cd_xSe/ZnSe$ and $ZnS_xSe_{1-x}/ZnSe$ measured relative to the Ni acceptor (filled $\triangle$) and Co ($\circ$, $\bullet$) donor levels for different temperatures: filled $\triangle$, $\circ$ — 2 K, $\bullet$ — 77 K, filled $\diamond$ — 300 K. The solid line is extrapolated from the TM averaging procedure for the corresponding binary compounds [4]. The value $E_c - 1.7$ eV for Co donor level in CdSe was taken from Ref. [9]. The data for 300 K are shifted down in the energy, which reflects a decrease in the fundamental band gap energies.

Fig. 3. Valence band offsets of $ZnMn_xSe_{1-x}/ZnSe$ measured relative to Ni acceptor level for $T = 2$ K. The data are taken from Ref. [5].

analysis, also. Absorption spectra were recorded by DFS-12 and Hitachi 340 spectrometers. Measurements were done at 2, 77 and 300 K. The observation of broad strong ionization absorption band in the range of 2.0–3.0 eV (Fig. 1) allowed us to estimate energy level positions of cobalt 2+/3+ charge state [8]. Band gap energies were determined either from exciton reflectivity spectra or calculated from the well-established $E_g(x)$ dependences. It was found that spectral dependence $\alpha(\hbar\omega-\hbar\omega_{th})^\beta$ describes well the spectra, when β instead of 1/2 (allowed process) or 3/2 (parity forbidden process) has some intermediate value, close to 1. It can be connected with a perturbation of the photoionization band by intra-d shell Co^{2+} transitions. The results of optical investigations are presented in Table and Fig. 2, together with our previous data on positions of valence and conduction band edges, measured relative to Ni 2+/1+ acceptor level.

TABLE

Composition x, energy gap E_g and a threshold energy $\hbar\omega_{th}$ for the Co photoionization (2+$\rightarrow$3+) in $Zn_{1-x}Cd_xSe$:Co and ZnS_xSe_{1-x}:Co alloys at 2 K.

Compound	x	E_g [eV]	$\hbar\omega_{th}$ [eV]
ZnSe:Co	0.0	2.82	2.49
$Zn_{1-x}Cd_xSe$:Co	0.01	2.81	2.48
	0.1	2.68	2.44
	0.2	2.60	2.2
	0.4	2.38	2.1
	0.5	2.34	2.05
ZnS_xSe_{1-x}:Co	0.05	2.84	2.56
	0.1	2.88	2.61
	0.3	3.03	2.66
	0.5	3.20	2.60
	0.9	3.68	2.66
	1.0	3.82	2.66

One can see that for CdSe/ZnSe values of band offsets obtained from the energies both Ni 2+/1+ and Co 2+/3+ photoionization transitions are very close to each other and for pure CdSe/ZnSe give the valence band offsets (0.1 ± 0.005) eV. It is near the values (0.13 ± 0.07) eV and (0.17 ± 0.01) eV determined by other methods [10], and predicted by the common anion rule. Previously obtained values of band offsets for another compound with cation substitution ZnMnSe/ZnSe [5] also demonstrate good agreement of our results (Fig. 3) with both theoretical calculations [11] and independent experimental data [12].

For compounds with anion substitution ZnSe/ZnSSe we got different values for the conduction band offset from Co 2+/3+ ionization energies, and from ones of Ni 2+/1+. At the first case it is equal to (0.17 ± 0.05) eV, and close to the

value 0.2, calculated by Harrison, and a number of experimental data [12]. From another side, a more pronounced shift of the conduction band ZnSe/ZnSSe, derived from Ni 2+/1+ photoionization energies, is relatively close to those obtained from the simple electron affinity rule [5], averaging procedure [4] and theoretical calculations [10].

Infra-shell transitions of Co^{2+} $(3d^7)$ are also modified with the change of the alloy composition (Fig. 1). We controlled changes with composition and temperature of three groups of transitions: $^4A_2(F) \to {}^4T_1(F)$, $^4A_2(F) \to {}^4T_1(P)$ and L, M and N lines at the Co photoionization threshold. All these bands show weak dependence on temperature. The effect of alloying on broadering and line shift is pronounced for L, M and N-lines, only. Their behaviour with an increase in Cd or S content is close to that of Ni^{2+} $^3T_1(F) \to {}^3T_2(F)$ and $^3T_1(F) \to T_2(G)$ transitions.

Concluding, we have determined energy level position of Co 2+/3+ charge state for a wide range of Cd and S fractions and temperatures in $Zn_{1-x}Cd_xSe$ and ZnS_xSe_{1-x} alloys. The estimated band edges for the valence and conduction bands are in relatively good agreement with our previous data, obtained from Ni 2+/1+ energy level position [5, 6], the theory and a number of experimental data for corresponding superlattices [12].

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