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ENERGY STATES IN THE SURFACE LAYER OF $Cd_{1-x}Mn_xSe$ FOR $0 \leq x \leq 0.10$*

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Surface photovoltage spectroscopy (SPS) measurements for $Cd_{1-x}Mn_xSe$ single crystals between 80 and 300 K at the pressure of 10^{-4} Pa were performed. The Fermi level energy was calculated. From the SPS curves the energy values connected with the electron transitions have been determined. Four types of effects have been stated: energy gap, shallow states close to the conduction band and two energy states connected with the structural defects, the native ones and those related to introduction of manganese into the CdSe matrix.

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The single crystal samples of $Cd_{1-x}Mn_xSe$ were grown from the melt using the Bridgman method by W. Giriat in IVIC, Caracas, Venezuela. The surface with orientation (100) was ground, polished with Gamal powder and rinsed in alcohol. The SPS measurements were carried out with a modified Kelvin method [1].

The $Cd_{1-x}Mn_xSe$ crystals are of the wurtzite structure. The valence band is split into two branches in the crystal field. The energy difference amounts to about 0.02 eV and decreases with increasing manganese content [2–4]. The more intense are the electron band-to-band transitions for the light polarized parallel to the x axis [2]. The presented results of the SPS measurements were obtained for the nonpolarized light, because the energy difference between the split edges of the valence band is comparable with the thermal broadening, especially at higher temperatures. The $Cd_{1-x}Mn_xSe$ crystals are of the native n-type [3]. Basing on the data presented in reference [5] the Fermi energy position was calculated. At room temperature it amounts to 0.04 eV for $x = 0$, 0.06 eV for $x = 0.05$ and 0.07 eV for $x = 0.10$. The Fermi level energy decreases nearly linearly with temperature and at 80 K reaches the same value for all investigated samples with various compositions x, and equals to 0.01 eV below E_c.

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The exemplary SPS curves for four various x values at the temperature of 250 K are presented in Fig. 1a. Two typical effects can be seen on all presented curves: increase in photovoltage in the range of 0.70–0.65 μm connected with the electron transitions from the valence to the conduction band, and the photovoltage quenching manifesting as a weak minimum on the background of the photovoltage increase. For the samples containing manganese also two increases in photovoltage arise for the longer wave range of 0.75–1.25 μm. They are connected with electron transitions from the energy states E_1 and E_2 to the conduction band. All observed electron transitions for the $Cd_{0.95}Mn_{0.05}Se$ sample at 250 K are presented in Fig. 1b. The energy values for all observed effects in the temperature range of investigations depend linearly on temperature according to the equation:

$$E(T) = E(0) + aT.$$

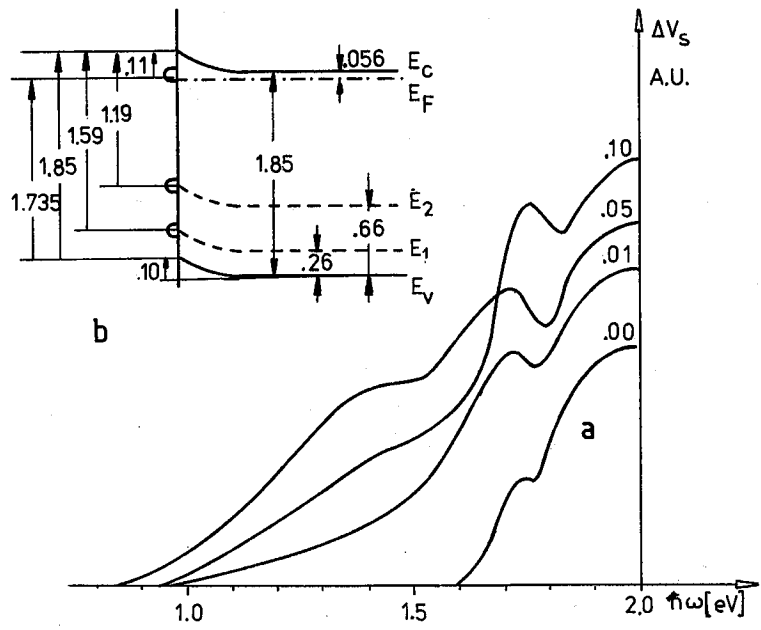

Fig. 1. a) Surface photovoltage spectroscopy curves at 250 K for $Cd_{1-x}Mn_xSe$ with $x = 0$, 0.01, 0.05, 0.10. b) Energy scheme of the $Cd_{0.95}Mn_{0.05}Se$ surface layer at 250 K. The energy values in eV.

TABLE I

Energy values of energy gap E_g , quenching effect E_q, photovoltage increases E_1 and E_2 at 200 K, and respective temperature coefficients a_g, a_q, a_1 and a_2 for various manganese contents x.

x	E_g (eV)	E_q (eV)	E_1 (eV)	E_2 (eV)	$a_g \cdot 10^4$ eV/K	$a_q \cdot 10^4$ eV/K	$a_1 \cdot 10^4$ eV/K	$a_2 \cdot 10^4$ eV/K
0	1.815	1.720	–	–	−0.41	−0.43	–	–
0.01	1.830	1.730	1.626	1.378	−0.53	−0.55	−0.55	−0.65
0.05	1.864	1.757	1.615	1.215	−0.42	−0.43	−0.61	−0.48
0.10	1.957	1.840	1.684	1.520	−0.67	−0.53	−0.49	−0.70

The energy values E at 200 K (the middle of the temperature range of experiments) and temperature coefficients a are listed in the Table I.

The temperature dependence of the energy gap E_g is similar to the results obtained with other methods [3, 4]. The quenching effect is connected with existence of the shallow states of energy $E_t = E_g - E_q$. The mean values of E_t amount to: 0.095 eV for x =0, 0.10 eV for $x = 0.01$, 0.11 eV for $x = 0.05$ and 0.10. These states can be of the surface but also of the bulk nature (donor states). Their energy is close to the Fermi level and they can be only partially filled at the equilibrium conditions. It is possible to fill them with electrons by illumination with photons of energy E_q. The states of energy E_1 are present mainly in the samples containing manganese. For CdSe ($x = 0$) a short tail exists in the longer wave range which can be attributed to the thermal broadening, but also to a low concentration of states with energy E_1. The states of energy E_2 do not exist on the SPS curves for CdSe. Therefore, they must be connected with the introduction of manganese into the samples. The similar effect was observed for $Cd_{1-x}Mn_xTe$ [6, 7], and it is of the structural nature. The effects at the energy of E_1 are probably connected with the native defects existing in CdSe [8] and $Cd_{1-x}Mn_xSe$ [5]. Introduction of manganese is disturbing the CdSe matrix and can cause increase in the native defect concentration and therefore the photovoltage increase at E_1 is more intense for the samples containing manganese. Because of similar structural nature of both effects at E_1 and E_2, the similar values of a_1 and a_2 are observed. These effects can not be related to electron transitions from the manganese levels to the conduction band, because they are situated inside the valence band [9, 10].

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