ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN — POLONIA
VOL. XLIII/XLIV,14 SECTIO AAA 1988/1989

Instytut Fizyki
Politechnika Wrocławska

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Surface Photovoltage Investigations of $Cd_{1-x}Mn_xTe$ Single Crystals

INTRODUCTION

The diluted magnetic semiconductors, and among them especially $Cd_{1-x}Mn_xTe$ are materials of a grate interest, their bulk properties are widely investigated. The papers on the surface properties of them however, are very scarce. In the presented paper the results of systematic studies, based on the surface photovoltage spectroscopy (SPS) experiments are presented. The SPS method yields information on the elctronic structure of the *surface layer and enables to determine the energy of the electron levels in the energy gap.* [1] . *Energy values of these levels can be obtained from the energetic positions of maxima of* $dV_s/d\lambda$ *on the SPS curves. There are three types of effects which can be observed on the SPS curves: increase in photovoltage which is connected with electron transitions from the valence band to the localized electron states; inversion of photovoltage relating to the electron transitions from the localized states to the conduction band; photovoltage quenching manifesting as a local minimum on the background of a strong increase (usualy connected with the band-to-band transitions) which is a result of inversion competitive to increase in photovoltage.*

EXPERIMENTAL

The $Cd_{1-x}Mn_xTe$ *single crystals with* $0 \leqslant x \leqslant 0.7$ *used for investigations were grown from the melt with the Bridgman method by W. Giriat in IVIC Caracas, Venezuela. The SPS measurements were performed in the temperture range between the liquid nitrogen and room temperature at the pressure* 10^{-4} *Pa, for the surface of (110) orientation. A modified Kelvin method with constant illumination was applied* [2] . *The measuring set ensured automatic tuning of the resonance frquency of the reference electrode vibration with temerature change, and practically constant sensitivity of the voltage measurements. The monochromator was equipped with NaCl or G-60 prism. As a light source were used a silit glow bar or a halogen lamp. All presented results are reduced to a constant illumination intensity for a given light source. The feeding conditions of the silit glow bar and halogen lamp were adjusted in such a way that the illumination intensities at the maxima of their spectral distributions were very similar. The dimensions of the single crystal samples amount to* $8x5x2\ mm^3$. *The surface with (110) orientation was ground polished with Gamal powder (Gamma Alumina A - 446) and rinsed in methanol and doubly deionized water. The electrical contacts were deposited on the sample by fusion of tellurium in a wacuum of* 10^{-4} *Pa.*

Three groups of effects had been found on the SPS curves *for $Cd_{1-x}Mn_xTe$ samples: shallow surface states which can be seen as increase in photovoltage in the far infrared region [3] or photovoltage quenching on the background of the band - to - band transitions (Figs 1,2 and 3); deep levels connected with manganese ions, giving increase in photovoltage, more and more intense with rising manganese content (Figs 4,5 and 6); acceptor levels present in $Cd_{1-x}Mn_xTe$, and manifesting on the SPS curves as strong inversion (Figs 7 and 8).*

DISCUSION

The investigated $Cd_{1-x}Mn_xTe$ samples were all of the native p-type. It is known from theory [4] that in the p - type wide band semiconductors can be present the shallow surface states with energy close to the valence band. The observed on the SPS curves quenching effects can be interpreted as the electron transitions from the filled surface E_t states to the conduction band on the background of electron transitions from the valence to the conduction band (Fig. 9). Electron concentration in the valence band is much bigger than in the surface states, therefore the increase in photovoltage is much more intense than inversion, giving in result the quenching effect. The E_t energy values depend on the way of the surface preparation [2] (experiments were performed for CdTe only), and on the manganese concentration x in $Cd_{1-x}Mn_xTe$. The energy values of the shallow surface states E_t for the mechanically polished samples are presented in table I.

Table I. Energy values of the shallow surface states E_t for various manganese contens x.

x	0	0.01	0.10	0.22	0.30	0.40
E_t (eV)	0.06	0.07	0.05	0.07	0.04	0.05

For manganese concentration $x > 0.4$ the E_t states were not observed.

On the SPS curves for $x \geq 0.01$ the photovoltage increase appears. It can be attributed to the electron transitions from

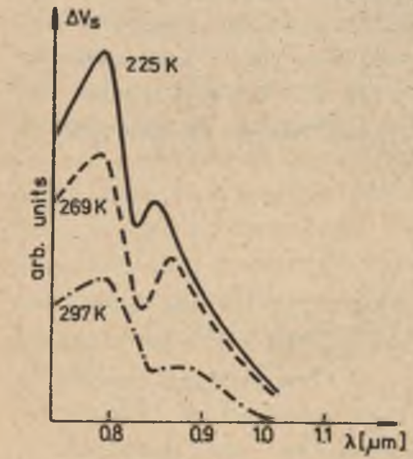

Fig. 1. Photovoltage quenching for CdTe, G-60 prism, silit glow bar.

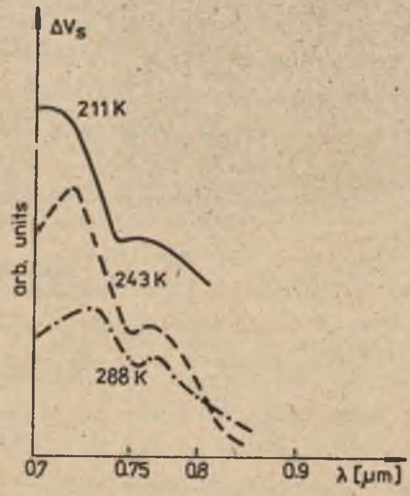

Fig. 2. Photovoltage quenching for $Cd_{0.85}Mn_{0.15}Te$, G-60 prism, silit glow bar.

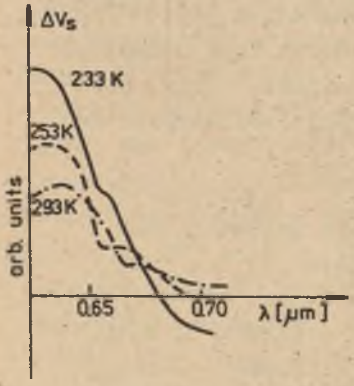

Fig. 3. Photovoltage quenching for $Cd_{0.70}Mn_{0.30}Te$ G-60 prism, halogen lamp.

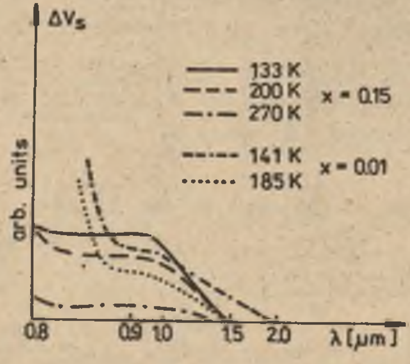

Fig. 4. Photovoltage increase for $Cd_{0.99}Mn_{0.01}Te$ and $Cd_{0.85}Mn_{0.15}Te$, NaCl prism, silit glow bar.

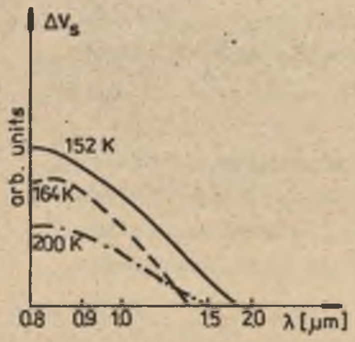

Fig. 5. Photovoltage increase for $Cd_{0.78}Mn_{0.22}Te$, NaCl prism, silit glow bar.

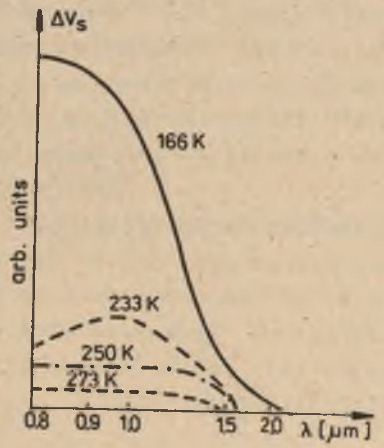

Fig. 6. Photovoltage increase for $Cd_{0.70}Mn_{0.3}Te$, NaCl prism, silit glow bar.

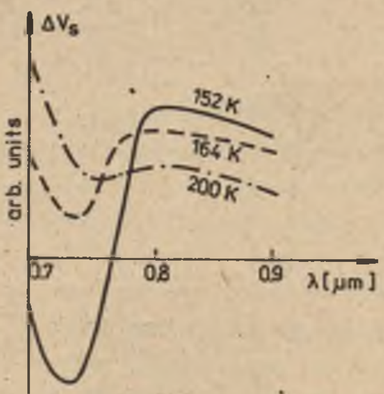

Fig. 7. Photovoltage inversion for $Cd_{0.78}Mn_{0.22}Te$, NaCl prism, silit glow bar.

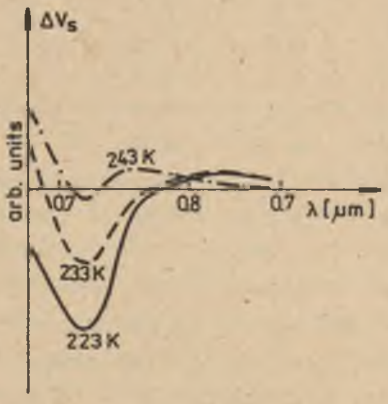

Fig. 8. Photovoltage inversion for $Cd_{0.70}Mn_{0.30}Te$, G-60 prism halogen lamp.

the valence band to the empty states with energy E_{Mn} near 1.0 eV over E_v. For $x \geq 0.60$, beside this level appears a second one with energy E'_{Mn}, about 2.3 eV over E_v. For x = 0.70 disappears the E_{Mn} level and remains the E'_{Mn} only. The energetic scheme of the surface layer of $Cd_{0.40}Mn_{0.60}Te$ is presented in Fig. 10. The energy values of E_{Mn} and E'_{Mn} states depend linearly on temperature according to equation:

$$E(T) = E(0) - a\ T$$

The temperature coefficients a_{Mn}, a'_{Mn} and a_g (index g relates to the energy gap) are of the same 10^{-4} eV/K order. Their values and E(0) values are listed in table II. The a_g and $E_g(0)$ values are in a good agreement with the data obtained with photoluminescence [5], optical absorption [6] and electroreflectance [7] measurements.

Table II. Temperature coefficients a and energy values E(0) for energy gap and manganese states.

x	$-a_g$ 10^{-4}eV/K	$-a_{Mn}$ 10^{-4}eV/K	$-a'_{Mn}$ 10^{-4}eV/K	$E_g(0)$ eV	$E_{Mn}(0)$ eV	$E'_{Mn}(0)$ eV
0.01	3.8	3.5	-	1.58	0.95	-
0.05	3.9	6.9	-	1.64	1.10	-
0.10	3.9	7.8	-	1.78	1.16	-
0.15	4.6	4.9	-	1.78	1.11	-
0.22	4.8	7.8	-	1.88	1.35	-
0.30	6.4	9.6	-	2.03	1.38	-
0.40	7.5	6.5	-	2.18	1.20	-
0.60	8.2	7.6	6.8	2.59	1.48	2.39
0.70	12.4	-	7.9	2.92	-	2.35

The nature of the E_{Mn} and E'_{Mn} levels is probably structural. Introduction of manganese into the CdTe matrix goes steply by exchanging the Cd with Mn ions. Substitution of cadmium by manganese disturbs the tetrahedral symmetry of the coordination polyhedron [8,9]. Such a disturbance can give in result a structural defect acting as an electron trap [10].

Inversion of the photovoltage on the SPS curves (Figs 7 and 8) can by attributed to the electron transitions from the *acceptor levels to the conduction band. The acceptor levels $E_A = E_g - E_{inv}$ determined from the SPS curves, listed in table III, agree well with data obtained with other methods [11, 12, 13] for x $\leq$ 0.20. For higher values of x, the transport methods [11, 12, 13] fail due to a very low electrical conductivity of the samples. In this situation the SPS is a unique method which enables to determine the energy of acceptor levels E_A.*

Table III. Acceptor level energies E_A for various manganese contents x.

x	0.01	0.05	0.10	0.22	0.30	0.40
E_A (eV)	0.15	0.14	0.16	0.20	0.26	0.35

For x $\geq$ 0.60 inversion on the SPS curves had not been found. The energetic scheme presenting all described electron processes for $Cd_{0.70}Mn_{0.30}Te$ at 230K is presented in Fig. 11.

For the samples with low concentrations of manganese there exist also other electron states of the surface nature, but they are described elsewhere [14].

CONCLUSIONS

Applying the surface photovoltage spectroscopy, the electron processes in the surface layer of $Cd_{1-x}Mn_xTe$ samples were investigated. Three types of the electron states in the surface layer were found: shallow surface states E_t, deep bulk states connected with manganese ions E_{Mn} and E'_{Mn}, and acceptor levels E_A of the bulk nature also. The energies of the shallow surface states are close to the valence band edge E_v. The E_t values ranges between 0.4 ÷ 0.7 eV over E_v and depend on the way of surface preparation and manganese content. The energies of the deep electron levels connected with manganese amount to about 1.0 eV for E_{Mn} and 2.3 eV for E'_{Mn}, over E_v. The acceptor level energies E_A are situated in the lower part of the energy gap and their values increase with increasing manganese content.

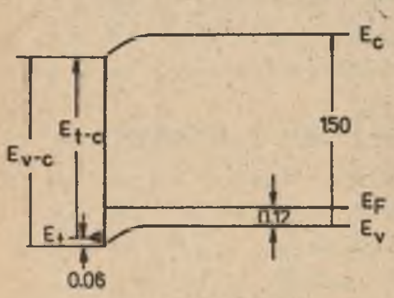

Fig. 9. Energetic scheme for the surface layer of CdTe at 269 K.

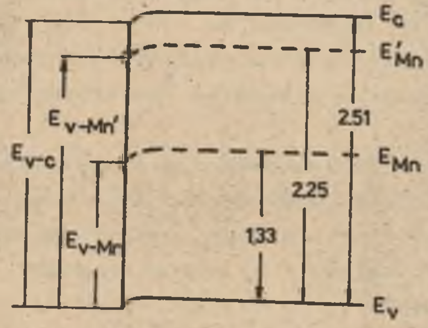

Fig. 10. Energetic scheme for the surface layer of $Cd_{0.40}Mn_{0.60}Te$ at 200K.

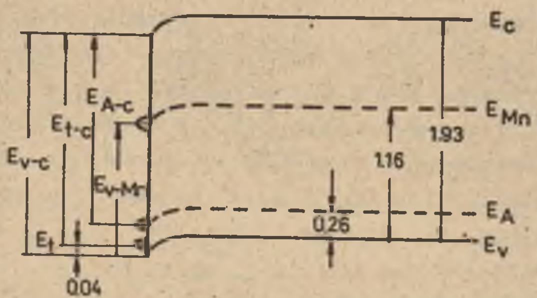

Fig. 11. Energetic scheme for the surface layer or $Cd_{0.70}Mn_{0.30}Te$ at 230K.

ACKNOWLEDGEMENT

The autors of the paper would like to thank prof. W. Giriat for the samples of the $Cd_{1-x}Mn_xTe$ single crystals. The investigations were sponsored by CPBP 01.08. C1-4.

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