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SURFACE ELECTRONOOPTICAL EFFECTS CONNECTED WITH GALLIUM DOPING OF $Cd_{0.85}Mn_{0.15}Te$

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Surface photovoltage measurements performed for the $Cd_{0.85}Mn_{0.15}Te$ single crystal samples intrinsic and gallium doped have shown influence of gallium doping on height and sign of the surface voltage barrier. From results of the surface photovoltage spectroscopy (SPS) measurements thevalues of acceptor, donor and manganese states energies have been determined. The photoconductivity (PC) measurements confirmed the effects found on the SPS curves.

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The intrinsic $Cd_{1-x}Mn_xTe$ single crystals are of *p*-type and in the normal equilibrium state the surface is positively charged and the energy bands are bent downwards [1, 2]. The energy value of the acceptor levels depends on manganese concentration x [2], and for $x = 0.15$ equals to 0.18 eV [3]. Doping with gallium introduces the donor states into the material and in the case of high enough concentration, the conductivity type of the sample can change from p to n.

The investigated $Cd_{0.85}Mn_{0.15}Te$, gallium doped single crystal samples were grown from the melt using the Bridgman method by W. Giriat in IVIC, Caracas, Venezuela. Before measurements the surface of (110) orientation was ground, polished with Gamal powder (Gamma Alumina A-446), rinsed in alcohol and deionized water. Surface photovoltage spectroscopy (SPS) was performed in the temperature range between 80 and 300 K, at a pressure of 10^{-4} Pa. The contact potential difference measurements between the semiconductor surface and gold reference electrode were carried out with a modified Kelvin method, ensuring aconstant sensitivity of voltage measurement in a wide range of temperature. The experimental details are described elsewhere [1]. The photoconductivity (PC) measurements were performed with a conventional method at the frequency of 4.8 Hz. The results are presented in Fig. 1.

The surface potential barrier height V_s^0 was determined from the photovoltage saturation after illumination with a white light. The dependence of V_s^0

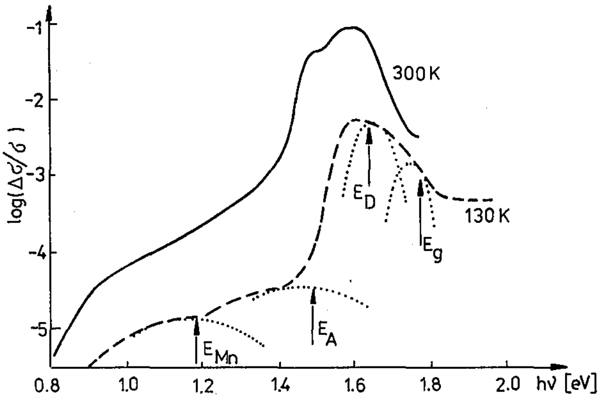

Fig. 1. Photoconductivity curves for 300 and 130 K.

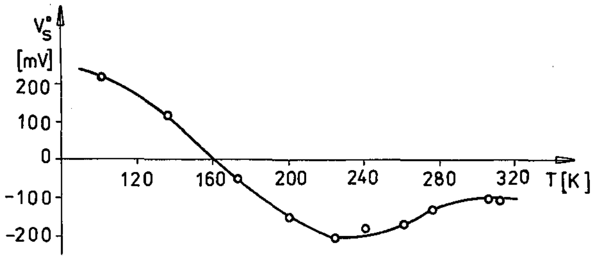

Fig. 2. Temperature dependence of the voltage barrier height V_s^0.

on temperature is presented in Fig. 2. In the range between the room temperature and about 160 K the voltage barrier is negative and the energy bands are bent upwards. At about 160 K the voltage barrier goes through zero and for lower temperatures changes its sign in positive. The SPS curves measuredusing the G-60 prism in monochromator and halogen lamp as a light source are presented in Fig. 3. All curves were obtained in the same conditions of the illumination intensity. The photovoltage changes presented on the SPS curves depend on the barrier height V_s^0. Therefore, the SPS curves for the temperatures of 243 and 233 K are the most developed. At 150 K (temperature close to 160 K, when $V_s^0 = 0$) on the SPS curve only a weak effect coresponding to the electron band-to-band transitions at the energy of E_g (0.7 μm) can be noticed. For the low temperature, at 86 K the SPS signal changes its sign, similarly as the surface voltage barrier.

Basing on analysis of the SPS curve for the temperature of 233 K the energetic scheme of the surface layer is proposed (Fig. 4). In intrinsic $Cd_{0.85}Mn_{0.15}Te$ samples there are the acceptor states of the energy $E_A = 0.18$ eV, and a wide band of the manganese states with a mean energy $E_{Mn} = 1.07$ eV [1]. For the gallium doped $Cd_{0.85}Mn_{0.15}Te$ sample the energy of the manganese states had

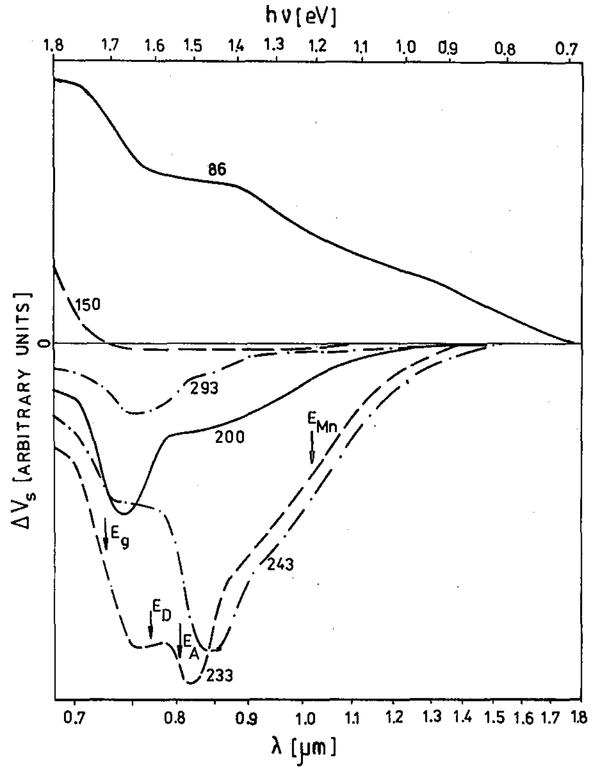

Fig. 3. Surface photovoltage spectroscopy curves at various temperatures, prism: G-60, light source: halogen lamp.

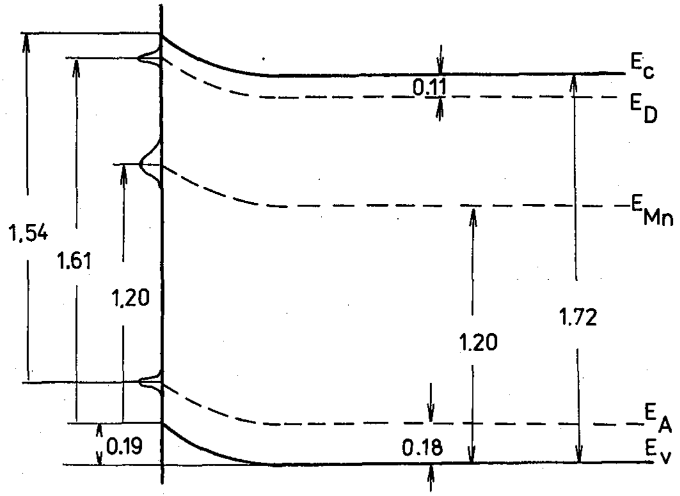

Fig. 4. Energetic scheme of the surface layer at 233 K.

been determined from the maximum of $dV_s/d\lambda$ for inversion of photovoltage in the range (0.9–1.2) μm. This inversion corresponds to the electron transitions from the valence band to the manganese states with the mean energy of 1.20 eV, and it is a little bigger than that for the intrinsic sample. At the energy close to 1.54 eV (0.8 μm) an increase in photovoltage appears corresponding with the electron transitions from the acceptor levels with energy $E_A = 0.18$ eV to the conduction band. The second inversion in photovoltage occurs at the energy of about 1.61 eV (0.77 μm). This effect is not present on the SPS curves for the intrinsic samples [1] and can be attributed to the electron transitions from the valence band to the gallium donor states. The energy of these states E_D is equal to the difference between $E_g = 1.72$ eV and 1.61 eV (energy of inversion) and amounts to 0.11 eV. This value agrees well with that given in Ref. [4], equal to 0.10 eV. The energy of the donor gallium levels in CdTe amounts to 0.05 eV [5]. One more difference between the intrinsic and gallium doped $Cd_{0.85}Mn_{0.15}Te$ samples consists in absence of the shallow surface states which are presented in the intrinsic material, close to the valence band [1]. Perhaps they are present also in the doped sample, but according to the theory [5] they should be situated between the conduction band and gallium donor states. In order to find them a better dispersion of the prism in this spectral range would be required.

The Fermi level position and gallium concentrationcould not be determined because the resistance of the sample was very high (10^5 Ω cm at the room temperature till 10^8 Ω cm at 130 K) and the Hall effect measurements could not be performed. It is very probable that the sample was compensated with a slight predominance of electrons as the free carriers, because the surface voltage barrier for the higher temperatures was negative. The shapes of the SPS curves, and especially that for 233 K point out that the Fermi level lies below the E_{Mn} states. So, they are empty and there are no electron transitions from them to the conduction band and on the SPS curve is not present any increase in photovoltage at 2.38 μm (0.52 eV). It is possible that for bigger gallium concentration the E_{Mn} states could be occupied.

The last effect of increase in photovoltage, close to 0.72 μm (1.7 eV) corresponds to the electron band-to-band transitions. The values E_g for the intrinsic and gallium doped samples are quite the same and similarly depend on temperature

$$E_g(T) = E_g(0) - aT.$$

The parameters of this linear equation determined from the SPS curves are: $E_g =$ 1.83 eV, $a = 4.2\times10^{-4}$ eV/K for the intrinsic sample, and: 1.82 eV, 4.2×10^{-4} eV/K for the gallium doped one.

The results of the PC measurements confirm the effects observed on the SPS curves. On the PC curves, and especially on those obtained at lower temperatures a wide band arises (Fig. 1) between 1.1 and 1.2 eV (manganese states), a shoulder at 1.50 eV (acceptor states) a broadening of maximum connected with energy gap, resulting from superposition of electron transitions from the valence band to the gallium donor states and band-to-band transitions.

The change of the sign of the voltage barrier at the low temperature corresponds probably to the adsorption processes. Inconditions of the technological vacuum (10^{-4} Pa), the rest gases exist inside the measuring chamber. It is known that H_2O and CO adsorbing on the surface of semiconductor can charge it positively [7]. The change of the sign of the surface voltage barrier from positive to negative with lowering of temperature was observed for the intrinsic $Cd_{1-x}Mn_xTe$ samples and was attributed to the negative oxygen ion adsorption [8]. But full interpretation of these effects needs further investigations.

Summarizing the presented results it can be stated that introduction of gallium into $Cd_{0.85}Mn_{0.15}Te$ sample changes the conductivity type from p in n and the voltage barrier becomes negative. The energy of the gallium donor levels amounts to 0.11 eV and the energy of the manganese states is a little bigger than for the intrinsic samples.

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