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Radiative and nonradiative recombination centers in Cl and Na doped CdTe monograin powders

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The wide 1.4 eV photoluminescence band, photoconductivity and dark conductivity of CdTe monograin powders were studied as a function of Na concentration. The donor-acceptor complex $Na_{Cd}Cl_{Te}$ is proposed as the radiative recombination center responsible for the 1.44 eV PL band as well as for the photoconductivity. The high *n*-conductivity of CdTe monograins with low Na concentration is determined by the ionization of shallow Cl_{Te} donor defects. The sharp decrease of the conductivity (10^7 times) in vicinity of equal concentrations of Na and Cl is due to the high level of compensation $Cl^{\bullet}_{Te} + e' + Na^{x}_{Cd} \rightarrow Na'_{Cd}Cl^{\bullet}_{Te}$. *© 2000 Kluwer Academic Publishers*

1. Introduction

CdTe is one of the most promising II–VI compounds for optoelectronic device applications [1]. In order to obtain suitable electrical and optical properties one should either grow stoichiometric impurity-free crystals [2, 3] or dope them with group III or VII donors and with group I or V acceptors [4–8]. Both due to the thermal treatment in the atmosphere of components at the elevated temperatures or due to the dissolved impurities a number of different point defects—single and complex—are formed [4–11]. These point defects, having local levels in forbidden gap, act as radiative and nonradiative recombination centers for electrons and holes [10]. They play significant role in forming photoluminescence (PL), photoconductivity (PC), dark conductivity (DC) and other characteristics of II–VI semiconductors [7–11]. Different methods can be used to identify the recombination centers with crystal lattice point defects: luminescence [1, 8], electron paramagnetic resonance (EPR) [1], optically detected magnetic resonance (ODMR) [12], quasichemical reactions [7, 9–11].

The 1.4 eV band is the most commonly observed PL band in CdTe [8]. PL bands observed in other wide gap II–VI semiconductor compounds, such as ZnS, ZnSe, CdS, CdSe, are relatively well separated. In CdTe some of them are grouped into relatively wide PL band at 1.4 eV [8, 10, 13–15]. One of these constituents is the SA-band. Centers of the SA-band are identified with good reliability as donor-acceptor complex defects consisting of an intrinsic acceptor—cation-site vacancy—in the nearest neighborhood of a donor impurity at the anion site (for example $V''_{Cd}Cl^{\bullet}_{S}$ in CdS or the so called A center in CdTe) [8, 16]. As for the nature of the other constituent subbands of 1.4 eV PL band there is still no unanimous general conception. The aim of the present research is to ascertain the nature of defects formed by dissolution of Cl and Na in CdTe monograins and appearing in the 1.4 eV PL band, photoconductivity and dark conductivity of samples with different concentrations of above mentioned impurities.

2. Experimental details

We used a vapour-phase synthesized initial CdTe powder containing residual impurities less than 10^{-5}%. The initial CdTe powder was heat-treated for 2 hours at 590°C in dynamic vacuum for removing possibly nonreacted separate phases of elements and for obtaining homogeneous starting material. Cadmium chloride was used as the solvent (fluxing material). The amount of flux (liquid solution of CdTe in solvent) was calculated on the base of phase diagram of CdTe-$CdCl_2$ taking into account that monograin growth mechanism is dominating only if the volumes of liquid and solid phases are nearly equal at the temperature of recrystallization [6]. Na was added as the water solution of NaCl. The added Na concentrations [Na] are given as relative to the initial amount of CdTe. One should consider that impurity concentration in final product may be less than the added initial concentration due to the distribution of a dopant between different phases in the closed system. Unfortunately the data for exact calculations are often unknown. The mixtures of CdTe with dopant and $CdCl_2$ were dried and annealed in sealed evacuated quartz ampoules in a preheated tube furnace at 750 °C for 14 hours. After isothermal annealing the ampoules were quenched to room temperature in deionized (DI) water. $CdCl_2$ flux was dissolved in DI water and the powders were multiply rinsed with DI water by decantation. Resistivity of materials was measured by pressing individual grains between two In contacts following the linearity of the V-A characteristics. The type of conductivity was determined by

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the thermo-probe method. Photoluminescence spectra measurements were carried out at 8 K using closed-cycle He cryostat. A He-Cd laser with the wavelength of 441.6 nm was used for excitation and a computer controlled 0.4 m single grating monochromator for PL measurements. The chopped signal was detected by a S1 photomultiplier using the conventional lock-in technique. For the purpose of analysis, the emission spectra were corrected for grating efficiency variations and for the spectral response of the detector.

3. Results and Discussion

In monograin technology the liquid phase of flux represents a source of doping impurities which are easily incorporated in the crystal growth process. The doping rate depends on the heating time and temperature and it is limited by the solubility of impurities in the conditions of sufficient amount of flux. In this work cadmium chloride was used as the fluxing material. So we have CdTe monograins with chlorine concentration probably equal to the solubility of chlorine in CdTe at 750 °C. We have determined the chlorine concentration in CdTe monograins grown at 650 °C in $CdCl_2$: $[Cl]_{sol} = 5.6 \times 10^{17}$ cm^{-3}. Concentration of added Na ([Na]) changes in the large region of 10^{16}–10^{21} cm^{-3}. Normalized spectra of PL of CdTe : Cl : Na are shown in Fig. 1.

The observed 1.4 eV PL band has nonsymmetrical shape without the phonon structure. Peak energy of this PL band shifts from 1.41 eV (10^{16} and 10^{18} cm^{-3} Na) to 1.44 eV (10^{17} and 5×10^{17} cm^{-3} Na), see Figs 1 and 2.

The half-widths of the band shows the same behavior: it increases from 0.086 eV (10^{16} cm^{-3} Na) to 0.11 eV (5×10^{17} cm^{-3} Na). It is obvious, that there becomes appearent (10^{17} cm^{-3} Na) a supplementary subband at the high energy wing of the 1.4 eV PL spectrum. The intensity of the 1.4 eV PL band increases with Na concentration from 10^{16} to 10^{17} cm^{-3} Na, then saturates and after that ($5 \times 10^{17} \rightarrow 10^{18}$ cm^{-3} Na) deeply decreases (Fig. 3). At [Na] $\geq 19^{19}$ cm^{-3} there appears a weak PL band with the maximum at 1.34 eV.

In the same Na concentration region of sharp decline of PL intensity (in vicinity of 10^{18} cm^{-3}) the conductivity decreases steeply by 6–7 orders of magnitude with simultaneous appearing of weak photosensitivity. Doubtless, the photoconductivity in the region of low [Na] is overshadowed by high dark conductivity which exceeds its value some 5–6 orders of magnitude.

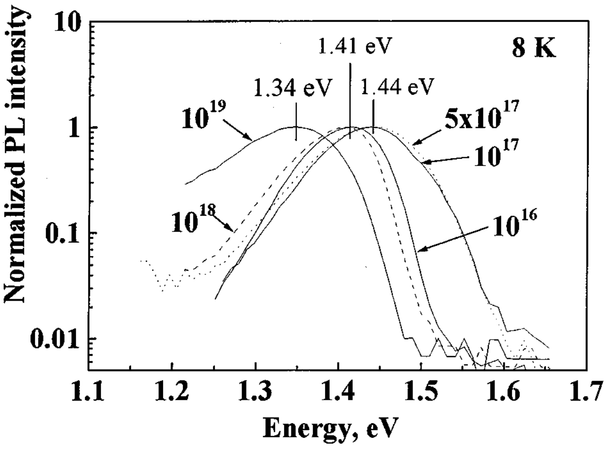

Figure 1 Normalized photoluminescence spectra of CdTe samples with different concentration of Na (cm^{-3}), measured at 8 K.

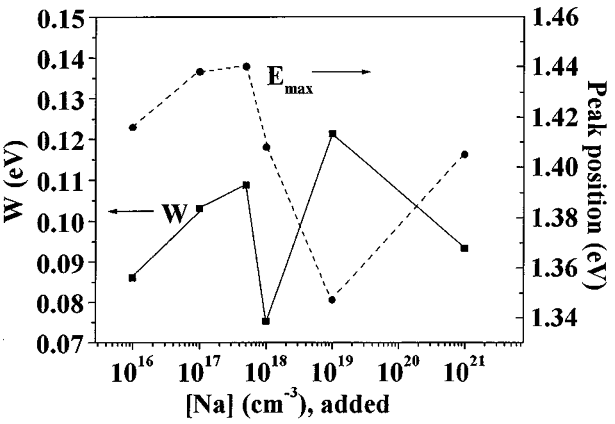

Figure 2 The Na doping dependencies of the peak position and the half-widths of the 1.4 and 1.34 eV PL band measured at 8 K.

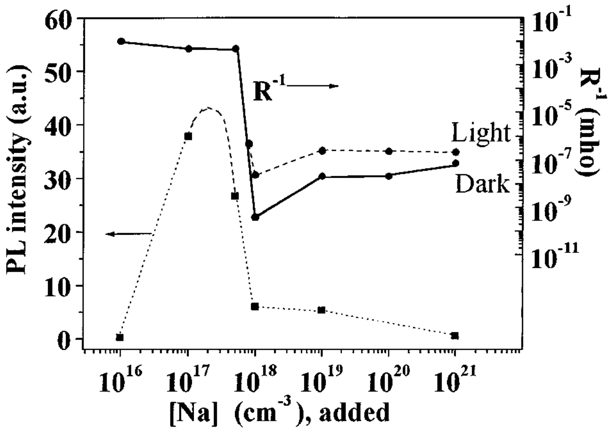

Figure 3 The Na doping dependencies of the 1.4 eV PL band intensity measured at 8 K and light and dark conductivities of CdTe measured at room temperature.

As it is well known, atoms of the group I elements (Li, Na, Cu) in the cation site of II–VI compounds form acceptor type centers like Cu'_{Cd} (charged state after the capture of an electron). At high concentrations, basing in the interstitial sites they form donor centers ($Cu_i^{\bullet}$). Atoms of the group VII elements displacing anions form donor centers ($Cl_{Te}^{\bullet}$) [7, 9–11, 15]. Due to the large ionic radius of group VII elements, the accommodation of Cl in the interstitial sites and formation of acceptor centers Cl'_i is less probable. The formation of donor-acceptor pairs of these impurity defects with intrinsic defects of crystal lattice or with each other is thermodynamically beneficial at high temperatures of sample preparation. At the same time the compensation of conductivity is going on: electrons escaped from donors into the conduction band are captured at acceptor levels.

So, we can consider the existence of following defects in our samples: Cl_{Te}, Na_{Cd}, Na_i, V_{Cd}, $V_{Cd}Cl_{Te}$, $Na_{Cd}Cl_{Te}$, $Na_{Cd}Na_i$, $V_{Cd}(Cl_{Te})_2$, $(Na_{Cd}Cl_{Te})_2$ and $(Na_{Cd}Na_i)_2$. The last three of them represent complicated complexes, the existence of which in II–VI compounds, especially in CdS, has been derived from the quasichemical analysis of the results of luminescence and high temperature conductivity [10, 11]. Above mentioned defects are formed at high temperature, at 750 °C in our case. At the temperatures of conductivity measurements (room temperature) and luminescence measurements (8 K) the atom defects are frozen-in and quasichemical reactions describe only electron (hole) transitions, which result in luminescence (radiative recombination of nonequilibrium electrons), in photoconductivity (photogeneration of electrons from the sensibility centers) or in dark conductivity (thermodynamical equilibrium between donors and C-zone). At low [Na] ($[\mathrm{Na}] \ll [\mathrm{Cl}] \approx 10^{18}\ \mathrm{cm}^{-3}$) the dark conductivity is determined by the equilibrium concentration of electrons in the conduction band, i.e. by the equilibrium of the reaction $\mathrm{Cl}^{x}_{\mathrm{Te}} \leftrightarrow \mathrm{Cl}^{\bullet}_{\mathrm{Te}} + \mathrm{e}' + \mathrm{E}_{\mathrm{D}}$, if the condition of electroneutrality is described by $n = [\mathrm{Cl}^{\bullet}_{\mathrm{Te}}]$. Due to the low ionization energy of chlorine donors $\mathrm{E}_{\mathrm{D}} = 14$ meV [16] we can consider that almost all of them are ionized: $[\mathrm{Cl}^{\bullet}_{\mathrm{Te}}] \gg [\mathrm{Cl}^{x}_{\mathrm{Te}}]$ and the concentration of free electrons is equal to the whole concentration of chlorine donors $n = [\mathrm{Cl}_{\mathrm{Te}}]$. This is providing the observed high dark conductivity. Due to the low concentration of acceptors V_{Cd}, $\mathrm{Na}_{\mathrm{Cd}}$ and donor-acceptor pairs formed by them, there is no remarkable compensation of conductivity. Low level of compensation of conductivity by $\mathrm{V}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}$ is mentioned in several works, for example in [16]. If the concentration of Na increases there is going on the intense formation of donor-acceptor pairs with the capturing of free electrons (at the high temperature of crystal growth):

$$\mathrm{Cl}^{\bullet}_{\mathrm{Te}} + \mathrm{e}' + \mathrm{Na}^{x}_{\mathrm{Cd}} \leftrightarrow \mathrm{Cl}^{\bullet}_{\mathrm{Te}} + \mathrm{Na}'_{\mathrm{Cd}} \leftrightarrow \mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}. \quad (1)$$

Since the formation of $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}$ is thermodynamically beneficial (contracting of the contrary charged defects), the concentration of $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}$ is much higher than the concentrations of $[\mathrm{Cl}_{\mathrm{Te}}]$ and $[\mathrm{Na}_{\mathrm{Cd}}] : [\mathrm{Na}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}] \gg [\mathrm{Cl}_{\mathrm{Te}}]$ and $[\mathrm{Na}_{\mathrm{Cd}}]$. This relationship will remain the same at low (room) temperatures where the atom defects are frozen-in. When the Na concentration is becoming equal to the chlorine concentration, $[\mathrm{Na}] \to [\mathrm{Cl}] \approx 10^{18}\ \mathrm{cm}^{-3}$, this results in the sharp decrease of dark conductivity, as it is seen in Fig. 3. The further increase of [Na] is accompanying with the high degree of selfcompensation by the formation not only $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}$, but also $(\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}})_2$ and $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i}$ and $(\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i})_2$. In the case of CdS : Cu : Cl the addition of Cu in amounts that exceed the solubility of Cl (without Cu) there is observed the effect of increased co-solubility of donor and acceptor impurities by formation of $\mathrm{Cu}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{S}}$ and $(\mathrm{Cu}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{S}})_2$ [9–11]. Probably the analogical processes take place also in our case of CdTe : Cl : Na.

The increase of the 1.4 eV PL band intensity by increasing Na concentration $10^{16} \to 10^{17}\ \mathrm{cm}^{-3}$ and shift of the peak energy from 1.41 ($10^{16}\ \mathrm{cm}^{-3}$ Na) to 1.44 eV (10^{17}–$5 \times 10^{17}\ \mathrm{cm}^{-3}$ Na) indicate the unambiguous influence of Na to the rise of the latter PL band. On the other hand, the saturation of the 1.44 eV band emission intensity in the region of $[\mathrm{Na}] \approx 5 \times 10^{17}\ \mathrm{cm}^{-3}$ (Fig. 3), where [Na] comes near to the [Cl], proves the participation of chlorine in formation of radiative centers responsible for this PL band: the deficit of $\mathrm{Cl}^{\bullet}_{\mathrm{Te}}$ limits the further growth of $[\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}]$. Analogically to wide bandgap II–VI compounds, where for main centers of impurity PL radiation are proposed donor-acceptor pairs (DAP) nearest neighbor or statistically distributed [10, 13–15, 17–19], we suppose $\mathrm{Na}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}$ as the radiative recombination center for the 1.44 eV band in CdTe : Cl : Na. Then radiative can be the transitions:

$$\mathrm{Na}^{x}_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}} + \mathrm{e}' \to \mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}} + h\nu$$

(free to bound recombination) (2)

or

$$\mathrm{Na}^{x}_{\mathrm{Cd}}\mathrm{Cl}^{x}_{\mathrm{Te}} \to \mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}} + h\nu'$$

(DAP recombination). (3)

Transitions like (2)—free to bound recombination and (3)—DAP recombination are well known in II–VI phosphors [10, 13–16, 20, 21]. As for the chemical nature of the center, transition like (3) in the similar pair of $\mathrm{Cu}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}$ is proposed to explain the 1.45 eV PL band in CdTe [22]. The location of the acceptor level of the donor-acceptor pair $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}$ in the forbidden band of CdTe is not known for us. There are data only for relatively isolated acceptor $\mathrm{Na}'_{\mathrm{Cd}}$, which level is 58.7 meV above the valence band [17]. In ZnSe PL bands located near 2.7 eV are connected with DAP emission of $\mathrm{Al}_{\mathrm{Zn}}\mathrm{Na}_{\mathrm{Zn}}$, $\mathrm{Al}_{\mathrm{Zn}}\mathrm{Li}_{\mathrm{Zn}}$ and $\mathrm{Li}_{i}\mathrm{Li}_{\mathrm{Zn}}$ [18]. In the case of high concentration of centers Krustok et al. [8] proposed an improved configurational coordinate model for the 1.4 eV PL band, in which the excited state of the recombination center is located within the conduction band. Thus, proceeding from our results and proposed models for impurity PL emission bands of other II–VI compounds (ZnS, ZnSe, CdS, CdSe), we can conclude that donor-acceptor pair $\mathrm{Na}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}$ serve as the center of 1.44 eV PL band in CdTe : Cl : Na. More complicated is the explanation of sharp decrease of 1.4 eV PL band intensity at $[\mathrm{Na}] \geq [\mathrm{Cl}] \approx 10^{18}\ \mathrm{cm}^{-3}$. It assumes a decrease of 1.44 eV PL emission centers and/or an increase of nonradiative recombination centers. The latter, having the high electron capture cross-section, play the role of the so called s-centers—rapid recombination centers, well known in CdS [23]. The nature of s-centers is not conclusivly determined, but there is an essential reason to associate them with double donor-acceptor pairs like $(\mathrm{Cu}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{S}})_2$ or $(\mathrm{Cu}_{\mathrm{Cd}}\mathrm{Cu}_{i})_2$ proposed for CdS on the base of quasichemical investigations of CdS : Cu : Cl [10]. Therefore, in our case we can suppose the going of following associative reactions at the high temperature of monograin powder preparation:

$$2\left(\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}\right) \leftrightarrow \left(\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}}\right)_2, \quad (4)$$

$$\mathrm{Na}'_{\mathrm{Cd}} + \mathrm{Na}^{\bullet}_{i} \leftrightarrow \mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i}, \quad (5)$$

$$2\left(\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i}\right) \leftrightarrow \left(\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i}\right)_2. \quad (6)$$

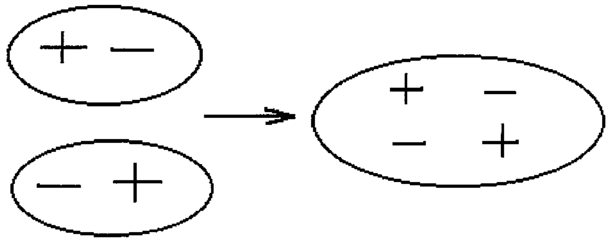

Figure 4 Schematic formation of a double pair complex.

The donor-acceptor pair is comparable with electrical dipole, which have "+" on donor and "−" on acceptor side. The process of association would go when donor-acceptor pairs of oppositely directed dipole moments shrink together in Coulomb field of their charges (Fig. 4).

Really, the impurity concentrations—[Na] and [Cl] would be higher than in the case of the homogeneous distribution of impurities in the crystals, because point defects are mainly located at extended defects, in the first order at dislocations [20, 24]. So, the average distance between the nearest DAP is sufficiently short for above mentioned Coulomb attraction. At the same time the rapid cooling of our samples may generate a significant number of dislocations in monograins. Therefore the main recombination stream is relocated to nonradiative channel of recombination and the PL emission intensities are remarkably decreased at $[\mathrm{Na}] \geq [\mathrm{Cl}] \approx 10^{18}\ \mathrm{cm}^{-3}$. It is the well known effect of the concentration quenching of PL emission.

At higher Na (and Cl) concentrations $[\mathrm{Na}] \approx 10^{19}\ \mathrm{cm}^{-3}$ there is observed a new broad PL band centered at 1.34 eV. Doubtlessly, it can not be the Z–PL emission of high purity *n*-type CdTe [20]. Which type of centers could cause such emission? Certainly, it has to have an impurity origin and to be connected with Na. Proceeding from the DAP origin of impurity PL emission in other II–VI compounds [18, 19], we may propose $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i}$ as the center responsible for the observed 1.34 eV PL emission band. $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i}$ is formed by reaction (5) and the PL emission may be generated by DAP recombination:

$$\mathrm{Na}^{x}_{\mathrm{Cd}}\mathrm{Na}^{x}_{i} \rightarrow \mathrm{Na}'_{\mathrm{Cd}}\mathrm{Na}^{\bullet}_{i} + h\nu'' \quad \text{(DAP recombination).} \tag{7}$$

Analogical to (7) radiative recombination of the center $\mathrm{Cu}_{\mathrm{Zn}}\mathrm{Cu}_{i}$ is observed in ZnS [18, 19] and in ZnSe [15].

Photoconductivity (Fig. 3) may be caused by the photogeneration of electrons from the sensibility centers to the C-zone. Analogically to CdS [10], $\mathrm{Na}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}$ may serve as the sensibility center in CdTe : $\mathrm{Na}'_{\mathrm{Cd}}\mathrm{Cl}^{\bullet}_{\mathrm{Te}} + h\nu \rightarrow \mathrm{Na}^{x}_{\mathrm{Cd}}\ \mathrm{Cl}^{\bullet}_{\mathrm{Te}} + \mathrm{e}'$.

4. Conclusions

High conductivity of quenched from 750 °C monograin powders CdTe : Cl : Na is caused by the ionization of chlorine donors $\mathrm{Cl}_{\mathrm{Te}}$. Sharp decrease of conductivity is connected with the high level of compensation of donors by acceptors with forming $\mathrm{Na}_{\mathrm{Cd}}\mathrm{Cl}_{\mathrm{Te}}$. The latter may be responsible for the 1.44 eV PL emission and for the photosensibility also. The 1.34 eV PL emission at $[\mathrm{Na}] \geq 10^{19}$ may be connected with DAP-recombination of $\mathrm{Na}_{\mathrm{Cd}}\mathrm{Na}_{i}$ centers.

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