

INFLUENCE OF A SURFACE TREATMENT ON THE ELECTRIC AND LUMINESCENT PROPERTIES OF CHLORINE-DOPED CdTe

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We investigate the influence of a surface treatment on the electric and luminescent properties of semi-insulating CdTe:Cl single crystals grown from the vapour phase. It is shown that the etching of CdTe:Cl samples in a 2% bromine-methanol etchant results in the change of the defect structure of their surface region, which is revealed in the essential decrease of the specific resistance and the spreading of the exciton bands of photoluminescence (PL). The treatment of the etched samples in a hydrogen gas discharge provides a partial recover of the quality of the near-surface region. In this case, the initial value of the electroconductivity of the CdTe:Cl samples is achieved, while the spreading of the PL exciton bands decreases.

An integral part of the process of manufacturing high-energy radiation detectors is the production of a high-quality surface. In order to remove a damaged layer formed due to the cutting of samples, one carries out a treatment of their surface: mechanical grinding, polishing, chemomechanical polishing, or chemical etching. This results in the deterioration of properties of the sample surface [3]. That's why, in order to avoid the shunting of the sample volumes in electric processes which can be a result of such a treatment, the sample surface is additionally passivated [4, 5]. For this purpose, one often uses hydrogen introduced into samples by various methods [6, 7].

1. Introduction

CdTe represents a well-known semiconductor material used for the production of uncooled detectors of X-ray and gamma radiation due to the combination of its physical properties important for this application (a large bandgap, sufficiently good transport properties, etc.).

A practical use of CdTe requires to possess structurally perfect crystals characterized by a specific resistance higher than 10^8 Ohm·cm. Lower values of the specific resistance induce too high leakage currents that essentially influence the detector property of CdTe-based devices [1]. However, CdTe grown with the use of any of the available technologies includes a high concentration of intrinsic uncontrolled defects which is higher than 10^{16} cm⁻³ according to the data given in [2]. That's why, in order to obtain a high specific resistance of cadmium telluride, it is doped with compensating impurities and, most often, chlorine or elements of the third group of the Periodic table of elements.

However, this results in the formation of additional trapping centers, which can result in a certain decrease of values of the lifetime and the mobility of charge carriers.

The given paper is devoted to the search of the possibilities allowing one to recover the surface of CdTe crystals damaged due to chemical etching. In this connection, we carry out the investigation of the electric properties and photoluminescence of CdTe samples etched in a 2% bromine-methanol etchant and treated in a hydrogen gas discharge.

2. Experimental Results and Their Discussion

In our investigations, we used semi-insulating ($\rho=10^9$ Ohm·cm) monocrystal CdTe:Cl samples (the chlorine concentration in the initial mixture $N_{Cl}=10^{19}$ cm⁻³). The doping by chlorine was fulfilled during the synthesis of a charge by adding CdCl₂ salt. The synthesis process and the growth method are described in papers [8,9]. The samples were obtained by means of the cleavage of the grown crystals of cadmium telluride along the (110) plane. After that, the crystals were subjected to free etching in the 2% bromine-methanol etchant during 30 s at 20 °C. Then, a part of the crystals was passivated by means of hydrogen treatment. The diffusion of hydrogen into the samples was fulfilled in a hydrogen gas discharge at a pressure of 0.25 Torr for 1 h at room temperature.

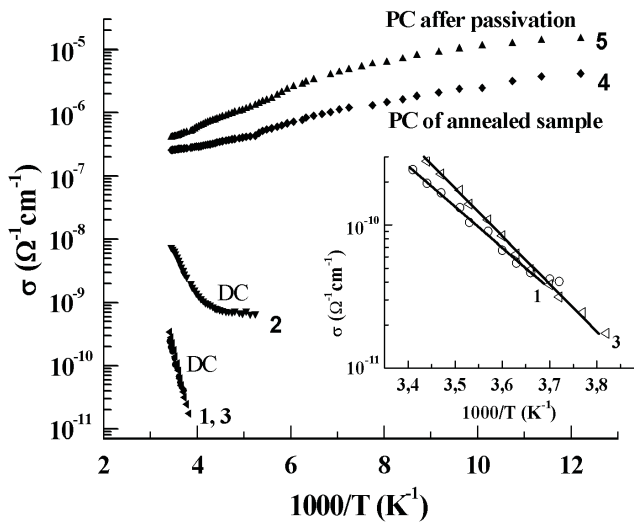


Fig. 1. Temperature dependences for CdTe:Cl ($N_{Cl} = 10^{19} \text{ cm}^{-3}$): 1 — dark conductivity of the initial sample; 2 — dark conductivity of the etched sample; 3 — dark conductivity of the sample hydrogenated after etching; 4 — photoconductivity of the etched sample; 5 — photoconductivity of the sample hydrogenated after etching

Figure 1 represents the temperature dependences of the electroconductivity of the initial sample (curve 1), electroconductivity (curve 2), and photoconductivity (curve 4) of the etched one, and electroconductivity (curve 3) and photoconductivity (curve 5) of the hydrogenated etched sample. One can see that the etching results in the appearance of two regions of the temperature dependences of the specific electroconductivity: in the temperature range 300–245 K, there appears a section with a slope of 0.4 eV, while the low-temperature region has a slope about 0.05 eV. In addition, due to the etching, the specific resistance of the crystals decreases (in some cases by an order of magnitude), which testifies to the fact that the surface shunts the current flowing through the sample. The treatment in a hydrogen discharge results in a partial recovery of the initial electroconductivity of the sample. The electroconductivity of the sample hydrogenated after etching and its temperature dependence acquire the nearly initial value and form. This dependence allows one to determine the activation energy of impurity-defect centers which amounts to 0.68 eV. This somewhat exceeds the activation energy of impurity-defect centers of the initial sample equal to 0.57 eV, which can be also related to the influence of the surface.

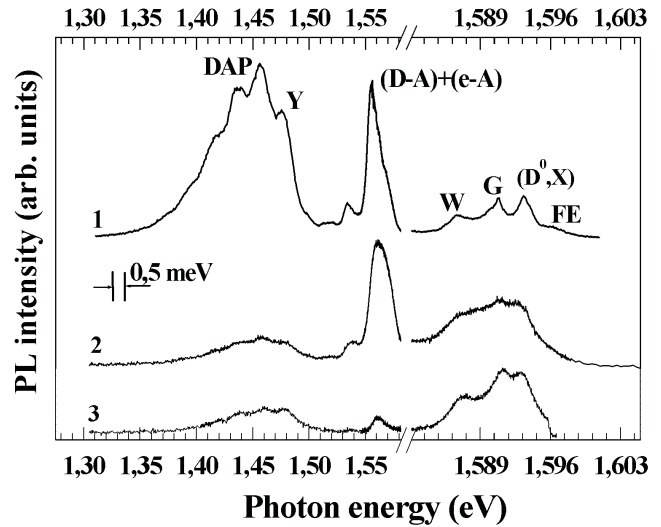


Fig. 2. Photoluminescence spectra of CdTe:Cl at $T = 5 \text{ K}$: 1 — initial sample; 2 — sample etched in bromine-methanol; 3 — sample hydrogenated after etching

Figure 1 also demonstrates that the photosensitivity of the investigated samples weakly depends on temperature. The heating from 77 to 300 K induces an inessential quenching of the photoconductivity (Fig. 1, curves 5 and 6), which testifies to a complexity of the recombination mechanism [10]. The behavior of the temperature dependence of the photoconductivity of the hydrogenated sample (Fig. 1, curve 4) is the same as that of the initial one, but, after the treatment in hydrogen, the value of the photoconductivity substantially increases.

Figure 2 shows the spectral dependence of the photoluminescence of the initial sample (curve 1), the etched one (curve 2), and the one hydrogenated after etching (curve 3) measured at 5 K.

The spectra of exciton photoluminescence of all the CdTe:Cl crystals presented in Fig. 2 include the bands with the maxima $\approx 1.593 \text{ (D}^0\text{X)}$, 1.590 (G) , and 1.586 eV (W) . Moreover, in the etched samples, they are very spread-out. According to the literature data [11], the first band is a result of the radiative recombination of excitons bound to shallow neutral donors (D^0X). The last are represented by Cl_{Te} substitutional atoms. The bands G and W are caused by the recombination of excitons bound to complexes of the acceptor type A_1 , $A_2 - (\text{V}_{\text{Cd}}^{-2} + 2\text{Cl}_{\text{Te}})$ and $(\text{V}_{\text{Cd}}^{-2} + \text{Cl}_{\text{Te}})^-$, respectively. The photoluminescence spectra of the initial sample (Fig. 2, curve 1) and the one hydrogenated after etching (Fig. 2, curve 3) also include a weak line of the radiation of free excitons (FE). This, along with a higher

sharpness of the bands of exciton PL in the hydrogenated samples as compared to the etched ones, testifies to the partial recovery of the quality of the crystal surface due to its treatment in hydrogen.

In the range 1.50 – 1.57 eV, the PL spectra of undoped CdTe contain a series of lines of the edge luminescence that consists of the principal line and its phonon replicas (Fig. 2). It is caused by two types of transitions: the high-energy component ($e-A_1$) corresponds to the electron transitions from the conduction band to shallow acceptor centers, while the low-energy one is associated with the transitions in donor-acceptor pairs ($D-A_1$). In ($D-A_1$), the donors are Cl_{Te} , and the acceptors are the complexes $(V_{\text{Cd}}^{-2} + \text{Cl}_{\text{Te}})^{-}$ [11]. For the investigated samples with a high dopant concentration, these components overlapped, by forming one radiation band. The principal feature of the edge luminescence of the hydrogenated samples is its low relative intensity that indicates a decrease of the concentration of acceptor centers.

The luminescence band at 1.45 eV is a result of the combination of two components: the radiation of donor-acceptor pairs (the donor is Cl_{Te} , the acceptor is the A -center $(V_{\text{Cd}}^{-2} + \text{Cl}_{\text{Te}})^{-}$) and the Y -line with their phonon replicas. The Y -band with the zero-phonon line at ≈ 1.477 eV is induced by the radiative recombination of excitons captured by the field of extensive defects. Its relative intensity is somewhat higher in the hydrogenated samples. However, as one can see from Fig. 2, the integral intensity of the 1.45-eV band in the etched (Fig. 2, curve 2) and hydrogenated (Fig. 2, curve 3) crystals is much lower than that in the initial CdTe:Cl crystal (Fig. 2, curve 1).

The presented temperature dependences (Fig. 1) demonstrate that, after the treatment of etched CdTe:Cl samples in a hydrogen gas discharge, the electric properties of their surfaces recover, which results in the increase of the specific resistance by more than an order of magnitude, up to the initial value of the cleaved crystals. This is evidently caused by the hydrogen passivation of shallow acceptor centers, whose ionization determines the behavior of the temperature dependences of the dark electroconductivity in the low-temperature region. Such a conclusion is also confirmed by the difference in the spectra of edge PL (Fig. 2, curves 2 and 3), whose relative intensity of radiation essentially decreases in the hydrogenated samples as compared to that in the etched one. The decomposition of the edge PL bands in the sum of

Gaussian functions according to the well-known formula [12] gives a possibility to determine the positions of the maxima of the ($e-A^0$) and ($D-A$) lines. For the hydrogenated sample, we obtained $E_{e-A^0}^{\text{H}} = 1.566$ eV and $E_{D-A}^{\text{H}} = 1.556$ eV, respectively, which coincides with the values of the maxima for the initial (freshly cleaved) sample, while, for the etched one, $E_{e-A^0} = 1.569$ eV, $E_{D-A} = 1.559$ eV. Such a shift is evidently associated with the strengthening of the Coulomb interaction between donors and acceptors due to an increase of the concentration of acceptor centers and a decrease of the distance between them. The theoretical substantiation of this fact is expressed by the formula [13]

$$h\nu = E_g - (E_A + E_D) + \frac{e^2}{\varepsilon R} + J(R).$$

The increase of the concentration of A_1 acceptor centers in the near-surface region of CdTe resulting from the etching in bromine-methanol is proved by the increase of the intensity of the ($e-A_1$) band (the short-wave wing of edge PL) — see Fig. 2, curve 2, as well as the increase of the dark conductivity of the etched sample (Fig. 1). The indicated changes become clear, if we take into account that the etching in bromine-methanol results in the depletion of the near-surface region of CdTe with Cd atoms, i.e. in the increase of the concentration of cadmium vacancies [3] which either behave as acceptors themselves or represent the constituents of acceptor complexes.

The improvement of the surface layer of samples treated in the hydrogen atmosphere is also confirmed by the presence of the line caused by the radiation of free excitons (FE) in the exciton region of PL of the hydrogenated samples as well as a higher clearness of the bands of bounded excitons.

Thus, the experimental investigations of the temperature dependences of the dark conductivity and photoconductivity, as well as the low-temperature photoluminescence of CdTe:Cl ($N_{\text{Cl}}=10^{19} \text{ cm}^{-3}$) single crystals etched in bromine-methanol with the following hydrogenization, demonstrate that:

- the etching of CdTe:Cl in bromine-methanol is accompanied with the enrichment of the sample surface with acceptors, most probably Cd vacancies;
- during the treatment of the etched samples in a hydrogen gas discharge, a part of the electrically active centers is passivated, which becomes apparent in the spectra of edge PL and photoconductivity as well as the

temperature dependences of the electroconductivity of the crystals under investigation.

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ВПЛИВ ОБРОБКИ ПОВЕРХНІ НА ЕЛЕКТРИЧНІ
ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ
НАПІВІЗОЛЮЮЧОГО CdTe,
ЛЕГОВАНОГО ХЛОРОМ

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Резюме

Досліджено вплив обробки поверхні на електричні та люмінесцентні властивості напівізолюючих монокристалів CdTe:Cl, вирощених із газової фази. Показано, що травлення зразків CdTe:Cl у 2%-вому бром-метаноловому травнику приводить до зміни дефектної структури їх приповерхневої області, що проявляється в значному зменшенні питомого опору та розмитті екситонних смуг фотолюмінесценції (ФЛ). Обробка протравлених зразків в газовому розряді водню дозволяє частково відновити якість приповерхневої області. При цьому відновлюється вихідне значення електропровідності зразків CdTe:Cl та зменшуються розмиття екситонних смуг ФЛ.