

## ON INTERACTION OF HYDROGEN ATOMS WITH COMPLEX DEFECTS IN CdTe AND ZnTe

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Low-temperature photoluminescence (PL) spectra of CdTe:Al and ZnTe single crystalline samples treated in a hydrogen gas discharge at  $T = 300$  K for 0.5 – 1.5 h are investigated. A model describing the relation of atomic hydrogen to complex defects ( $V_{\text{Cd/Zn}}^{2-}D^+$ ) and ( $V_{\text{Cd/Zn}}^{2-}2D^+$ ) in  $n$ -CdTe and  $p$ -ZnTe crystals is constructed. It is shown that the interaction of hydrogen with complex defects results in their decay and the passivation of one of the components. It is found that there occurs the passivation of donors in CdTe:Al ( $N_D > N_A$ ) samples and acceptors in ZnTe ( $N_A > N_D$ ), which induces the electric activity of the non-passivated components. This fact is in accordance with the investigations of PL at 5 K and the temperature dependences of electroconductivity.

In the last years, there appeared a number of publications devoted to studying the influence of hydrogen on physical properties of CdTe and ZnTe [4–12]. It was found that hydrogen can play an important positive role affecting the physical activity of many structural defects and extraneous uncontrolled impurities. That's why the investigation of the interaction of these defects with hydrogen is not only of scientific interest but also of practical importance.

However, it turns out that the efficiency of the passivation phenomenon depends on many factors, namely on the state of the crystal surface, temperature, hydrogen pressure, diffusion time of hydrogen, etc. Each of these factors is insufficiently investigated. At the same time, by introducing hydrogen into a crystal, one doesn't always obtain a desired result. For example, the introduction of hydrogen is accompanied by an increase in the specific resistance or by the complete passivation of structure-impurity centers not in every sample. The given paper is devoted to the investigation of some of these factors.

### 1. Introduction

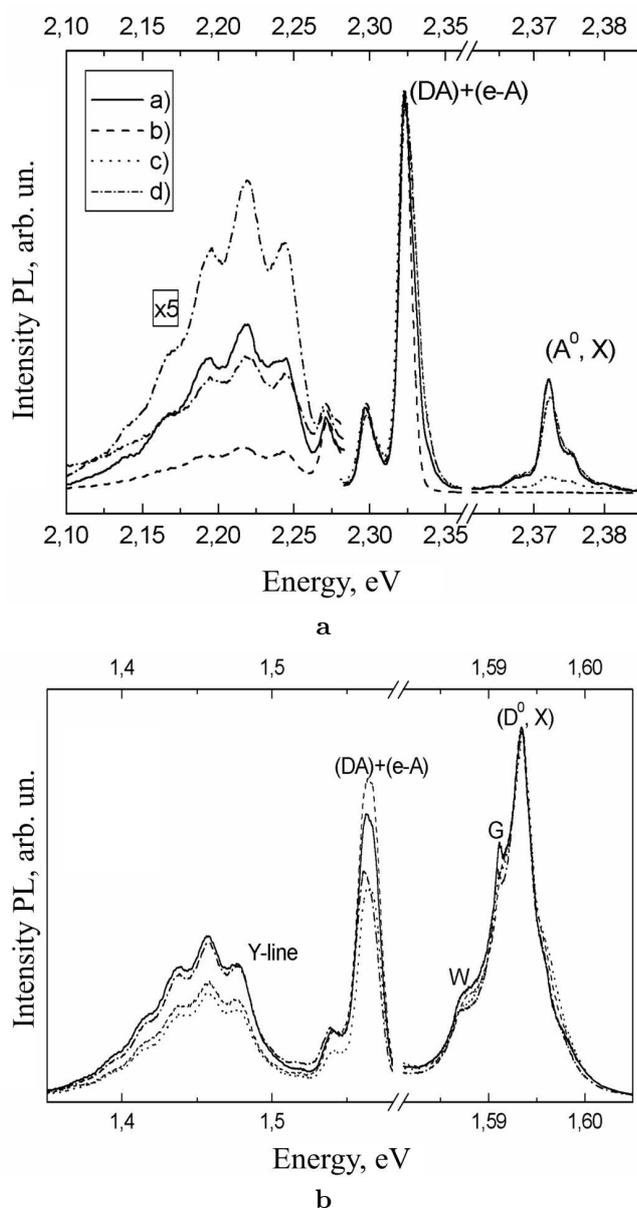
Large bandgaps of CdTe (1.5 eV at 300 K) and ZnTe (2.26 eV at 300 K) set the conditions for their use for the development of ionizing-radiation detectors, fast-operating optical switches, etc. In addition, ZnTe is used as a barrier material in the production of various low-dimensional structures on the basis of  $A^2B^6$  semiconductor compounds.

Thus, the increasing use of semiconductors in electronic engineering raises requirements to the technology of their fabrication. In particular, the growing of crystals with a low concentration of structural defects and dislocations remains an important problem. In order to grow semiconductors characterized with a high melting temperature, one often uses the method of sublimation. Recently, much attention has been paid to the investigation of the influence of hydrogen on properties of semiconductors. The interest of researchers is attracted by the fact that, with the help of hydrogen, one can improve electrophysical characteristics of semiconductors. Atomic hydrogen has a specific property to actively interact with various point defects and impurities and to form neutral D–H-complexes (defect-hydrogen), which is equivalent to the effective “purifying” of a material [1–3].

### 2. Experimental Results and Their Discussion

The investigated ZnTe and CdTe samples were grown using the sublimation method at temperatures of 1075 and 980 °C, respectively. Specially undoped ZnTe samples had the  $p$ -type of conduction with a concentration of holes of the order of  $10^{12}$  cm<sup>-3</sup> at a temperature of 300 K. CdTe was doped with aluminum (the concentration of Al  $\approx 10^{18}$  cm<sup>-3</sup>). All the investigated samples were monocrystals. The measurements were carried out at cleavages.

Hydrogen was introduced into the samples from a gas discharge at room temperature. The time of treatment was varied from 0.5 to 1.5 h. As the purpose of the given investigation was to study the influence of hydrogen on physical properties of ZnTe and CdTe depending on



Photoluminescence of ZnTe (a) and of Al-doped CdTe (b) at 5 K: a) initial sample; b) sample treated in hydrogen discharge for 0.5 h; c) 1.0 h; d) 1.5 h

the time of interaction between hydrogen and a crystal, the pressure of hydrogen in the setup was maintained constant.

The spectra of low-temperature ( $T = 5$  K) PL were investigated on an automatized setup consisting of an excitation source (a continuous Ar-laser LGN-503), helium cryostat, spectral device (MDR-23), photodetector produced on the basis of a photoelectronic multiplier FEU-62, amplifier, and personal computer.

Figure 1 presents PL spectra at 5 K for ZnTe and CdTe samples, respectively. The given spectra are typical of PL of these semiconductors.

In the exciton region of the PL spectrum for ZnTe samples, one observes the weak radiation of free excitons with a peak energy of 2.380 eV that disappears after the treatment of ZnTe in hydrogen for 0.5 h. With increase in the treatment duration, one again observes a weak radiation line in the exciton region of PL that somewhat grows with treatment time. In the exciton region, one observes a radiation band at about 2.375 eV that is associated with the radiation of excitons bound to neutral donors ( $D^0$ , X). Donors in undoped ZnTe can be presented by uncontrolled impurities belonging to group III or VII that substitute Zn or Te atoms, respectively. The wide band related to the radiative recombination of excitons bound to neutral acceptors ( $A^0$ , X) with the maximum at 2.372 eV is the most intense one.

As one can see from Figure, a radiation in the exciton region of ZnTe treated in hydrogen during 0.5 h is practically unobservable, while, after the 1-h treatment, it is rather weak. As the treatment duration rises to 1.5 h, the intensity of PL in the exciton region increases (almost up to the intensity of the untreated sample), and the radiation peak somewhat shifts to the side of higher energies.

The edge PL of zinc telluride observed in the spectral range 2.260–2.350 eV is related to the presence of shallow acceptors and shallow donors in the crystal. Such a PL is caused by two types of transitions: the electron transitions from the conduction band to shallow acceptors ( $e-A^0$  band) and donor-acceptor ones ( $D-A$  band). The energy distance between the  $e-A^0$  and  $D-A$  bands depends on the concentration of donors and acceptors, and these bands are weakly resolved, as a rule. The decomposition of the ( $e-A^0 + D-A$ ) band into Gaussian components gives a possibility to determine the radiation energies of the ( $e-A^0$ ) and ( $D-A$ ) bands. In the long-wave region, one observes two phonon replicas of this band.

In the edge region of the spectra in the samples treated in hydrogen for 0.5 h, the radiation band acquires a more symmetric form. This fact is probably caused by a decrease of the contribution of the ( $e-A^0$ ) band to the edge radiation band after the 0.5-h treatment in hydrogen.

At low excitation levels, the ionization energy of acceptors  $E_A$  can be determined by the formula [13–15]

$$E_{e-A} = E_g - E_A + kT/2.$$

The activation energy of an acceptor determined in such a way testifies to the fact that, in all the investigated ZnTe samples, the same acceptor with the energy  $\approx 67.5$  meV takes part in the ( $e-A^0$ ) radiation, which agrees with the energy level of 62.0 meV determined by the temperature dependence of electroconductivity. In the literature, somewhat lower energies are presented:  $\text{Li}_{\text{Zn}} = 60.6$  meV,  $\text{Na}_{\text{Zn}} = 62.5$  meV, and  $\text{P}_{\text{Te}} = 63.5$  meV [16].

With regard for the energy of the acceptor, the energy of the donor in hydrogenated samples changes from 2.90 meV at  $t = 0.5$  h to 5.21 meV at  $t = 1.5$  h. In this case,  $E_D = 3.73$  meV in untreated samples. Probably, such an ambiguous determination of the donor energy is related to a change of the donor-acceptor interaction radius in ( $D-A$ ) which depends, in turn, on the concentration of donors.

The wide band 2.210–2.250 eV is associated with the radiative recombination of donor-acceptor pairs (DAP) with participation of longitudinal optical phonons, which is confirmed by the presence of replicas of the zero-phonon line (with the distance between their maxima equal to the energy of the longitudinal optical phonon in ZnTe  $h\nu_0 = 25.5$  meV). In the given region of PL, there appears a zero-phonon radiation line of DAP with a peak at 2.245 eV, while one observes 1LO, 2LO, and 3LO phonon replicas in the long-wave side of this line. As one can see from Fig. 1, *a*, after 0.5-h treatment of ZnTe in hydrogen, the 2.210–2.250 eV band is the least intense one. As was already noted, in ZnTe hydrogenated for 0.5 h, radiation in the exciton PL region disappears almost completely. In this case, the ratio of the radiation intensities of the ( $e-A^0$ ) and ( $D-A$ ) bands amounts to 0.164, which represents the least magnitude. Taking this fact into account, one can assume that, after 0.5-h treatment in hydrogen, the concentration of electrically active acceptors in ZnTe samples abruptly decreases, which results, in turn in the low concentration of DAP. Such an effect can be caused by hydrogen passivation of electrically active acceptor centers.

The band with the maximum at 2.270 eV isn't identified. In all the investigated samples, the radiation intensity of this band is almost the same. Only in samples treated for 0.5 h, its maximum shifts to the short-wave region by 2.3 meV. This band in CdTe is considered to be the *Y*-band [15]. The total PL spectrum of CdTe is formed by both radiative recombination of DAP, where acceptors are presented by dopant substitutional atoms or *A*-centers, and  $D^0h$ -deep-donor recombination or recombination of excitons bound to dislocations (*Y*-band). It is supposed that the behavior

of this band corresponds to the case of the recombination radiation of excitons captured by extensive defects.

It's obvious that a similar situation takes place in ZnTe: for radiative transitions, *A*-center ( $(V_{\text{Zn}}-D_{\text{Te}})$  complex) represents an acceptor, while the shallow donor is presented by an uncontrolled impurity center.

Thus, CdTe and ZnTe belong to defect semiconductors, in which, along with point defects, complex defects are formed due to self-compensation. For example, due to self-compensation, metal vacancies  $V_{\text{Cd}}$  in CdTe combine with donors into complex defects ( $V_{\text{Cd}}^{2-}D^+$ ) and ( $V_{\text{Cd}}^{2-}2D^+$ ). In the same way, defects of a similar structure are also formed in ZnTe, which is energetically advantageous.

The introduction of hydrogen into crystals changes the PL spectrum. Its influence on the recombination radiation system is observed in each of its parts: exciton, edge, and impurity ones. In the exciton part of the spectrum of the investigated CdTe:Al samples, hydrogen influences the *W* and *G* bands which are associated with ( $V_{\text{Cd}}^{2-}D^+$ ) and ( $V_{\text{Cd}}^{2-}2D^+$ ) complexes, respectively. On these bands, excitons are localized. The intensities of the *W* and *G* bands decrease depending on the time of treatment of a sample in hydrogen (Figure, *b*).

In the edge region of PL of Al-doped CdTe, the highest intensity of radiation is observed in the case of 0.5-h treatment of samples in hydrogen. With increase in the treatment time, it decreases. In the impurity region of PL (1.350–1.500 eV), one can observe the minimal intensity of radiation in the case of 1-h treatment of samples in hydrogen. With a further increase in the time of hydrogen diffusion up to 1.5 h, the intensity of radiation approaches the initial value.

Analyzing the band of edge PL in CdTe, in particular, decomposing it into Gaussian components, one obtains the maximum of radiation of the ( $eA^0$ ) component. It gives a possibility to determine the acceptor level position. The energy position of this level in the bandgap is equal to 46 meV and agrees with the ionization energy of the acceptor center ( $V_{\text{Cd}}^{2-}2D^+$ ) [17]. Thus, these complex defects participate in CdTe PL. From the literature, it's known [13] that the change of the intensity of the edge and exciton PLs is determined by the concentration of  $V_{\text{Cd}}$ , and the PL intensity increases with its growth.

Thus, the dependence of the PL spectrum on the time of hydrogen diffusion into samples is practically determined by the interaction of hydrogen with native point and complex defects.

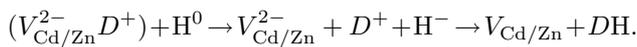
We assume that the difference in the behavior of the lines of recombination of excitons bound to ( $V_{\text{Cd}}^{2-}D^+$ )

and  $(V_{\text{Cd}}^{2-}2D^+)$  centers is caused by a change of the concentrations of these centers, which can take place due to the decay of the complexes under their interaction with hydrogen.

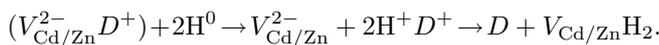
Such an assumption is substantiated by a decrease of the concentration of  $(V_{\text{Cd}}^{2-}D^+)$  and  $(V_{\text{Cd}}^{2-}2D^+)$  centers indicated by  $W$  and  $G$  bands in CdTe, the dependence of the radiation bands on the time of treatment of the crystals in hydrogen (practically on the hydrogen concentration), the absence of excitons in the exciton region in ZnTe samples treated in hydrogen for 0.5 h and their further appearance, etc.

Let's consider some models of the interaction of hydrogen with impurities and defects in semiconductors. It's known [6] that hydrogen passivates impurities and defects making them electrically neutral. A lot of properties of crystals can be explained based on the models presented below.

Let the concentration of donors in CdTe or ZnTe be higher than the concentration of acceptors,  $N_D > N_A$ . That is, an  $n$ -semiconductor is considered. The Fermi level lies higher than the level of hydrogen in the bandgap. When hydrogen enters into a semiconductor, it can attach an electron and becomes  $H^-$ . Due to the Coulomb interaction, a negatively charged hydrogen ion  $H^-$  and a positively charged donor  $D^+$  form a neutral complex  $(D^+H^-)$ . In this case, the donor is passivated, and the crystal can acquire the  $p$ -type conduction due to the reaction



If a crystal has the  $p$ -type of conduction, and the concentration of acceptors is higher than that of donors,  $N_A > N_D$ , then the Fermi level lies lower than the hydrogen level position. Into a crystal neutral hydrogen  $H^0$  acquires the properties of a donor. In this case, there appears a possibility for both the passivation of an acceptor by hydrogen and the formation of an electrically neutral complex  $(A^-H^+)^0$  according to the reaction



Thus, in the case of the interaction of hydrogen with complex defects, they finally dissociate, which results in a change of both the concentration of acceptors or donors and, consequently, the electrical and optical properties of crystals.

The release of zinc vacancies caused by the interaction of hydrogen with defects also manifests itself in the PL spectrum. In particular, one observes an

increase of the PL intensity in the edge region of PL. Though the presented model of the interaction of hydrogen with complex defects explains the growth of electroconductivity in CdTe:Al and ZnTe hydrogenated samples, it is still approximate as the spectrum of defects in these semiconductors is more complex than that presented by the discussed models.

### 3. Conclusions

Based on the investigations of PL of  $n$ -CdTe and  $p$ -ZnTe crystals, a model of the interaction of atomic hydrogen with point and complex defects in these crystals is proposed. It is shown that the interaction of hydrogen with complex defects results in their dissociation and passivation of separate components: donors – in  $n$ -semiconductors and acceptors – in  $p$ -semiconductors, which is determined by the position of the Fermi level with respect to the energy level of hydrogen. This dependence determines the charge of hydrogen and the passivation of some impurities and defects.

1. E.M. Omel'yanovskii *et al.*, Fiz. Tekhn. Polupr. **23**, 178 (1989).
2. D.G. Letenko, E.V. Molodtsova *et al.*, Fiz. Tekhn. Polupr. **25**, 2123 (1991).
3. S.J. Pearton, J.W. Corbrtt, and J.T. Borenstein, Physica B **170**, 85 (1991).
4. S. Bhunia, D. Pal, and D.N. Bose, Semicond. Sci. Techn. **13**, 1434 (1998).
5. N. Guergouri, N. Brihi, Y. Marfaing, R. Triboulrt, J. Cryst. Growth **256**, 230 (2003).
6. D. Mathiot, Phys. Rev. B **40**, 5867 (1989).
7. P.R. Berndt, J.H. Neething, C.B. Franklyn, and H.W. Zandbergen, Mater. Sci. Eng. B **113**, 253 (2004).
8. U. Reislohner, N. Achtziger, C. Hulsén, and W. Witthuhn, J. Cryst. Growth **214/215**, 979 (2000).
9. J. Hamann, D. Blab, A. Burchard, and C. Casimir, J. Cryst. Growth **184/185**, 1147 (1998).
10. J. Jaglarz, B. Pukowska, A. Kisiel, and J. Olejniczak, J. Al. Compound. **371**, 125 (2004).
11. S. Mergui, M. Hage-Ali, J.M. Koebel, and P. Siffert, Nucl. Instrum. Meth. Phys. Res. **A322**, 381 (1992).

12. D.V. Korbutyak, N.D. Vakhnyak, D.I. Tsutsura, O.M. Pihur, and P.M. Peleshchak, *Ukr. Fiz. Zh.* **52**, 378 (2007).
13. A.V. Kvit, S.A. Medvedev, Yu.V. Klevkov, V.V. Zaitsev *et al.*, *Fiz. Tverd. Tela* **40**, 1010 (1998).
14. D.V. Korbutyak, S.G. Krylyuk, Yu.V. Kryuchenko, and N.D. Vakhnyak, *Optoelectr. Polupr. Tekhn.* **37**, 23 (2002).
15. H. Tews, *Phys. Rev. B* **23**, 587 (1981).
16. Le Si Dang and R. Romestain, *Solid State Commun.* **43**, 829 (1982).
17. S.H. Song, J. Wang, Y. Ishikawa, S. Seto, and M. Isshiki, *J. Cryst. Growth* **237/239**, 1726 (2002).

ПРО ВЗАЄМОДІЮ АТОМІВ ВОДНЮ ІЗ СКЛАДНИМИ ДЕФЕКТАМИ В CdTe І ZnTe

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Резюме

Досліджено спектри низькотемпературної фотолюмінесценції (ФЛ) монокристалічних зразків CdTe:Al і ZnTe, оброблених в газовому розряді водню при  $T=300$  К протягом 0,5–1,5 год. Побудовано модель взаємозв'язку атомарного водню із складними дефектами ( $V_{\text{Cd/Zn}}^{2-}D^+$ ) і ( $V_{\text{Cd/Zn}}^{2-}2D^+$ ) в кристалах  $n$ -CdTe і  $p$ -ZnTe. Показано, що взаємодія водню із складними дефектами приводить до їх розпаду і пасивації одного із компонентів. Отримано, що в зразках CdTe:Al ( $N_D > N_A$ ) пасивуються донори, а у зразках ZnTe ( $N_A > N_D$ ) зазнають пасивації акцептори, що і приводить до електричної активності непасивованих компонентів. Це підтверджується дослідженнями ФЛ при 5 К і висновками з температурних залежностей електропровідності.

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