ON HYDROGEN-STIMULATED PASSIVATION OF ELECTRICALLY ACTIVE CENTERS IN $Cd_x Zn_{1-x}Te$

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An influence of hydrogen on electrical properties of $Cd_xZn_{1-x}Te$ crystals with several values of x has been studied. Hydrogen has been shown to passivate shallow-level acceptor centers in crystals with conductivity of the p type, which may stimulate a growth of the specific resistance in low-resistance crystals by several to 10^3 times. In high-resistance compensated crystals, penetrated hydrogen results in a substantial reduction of their specific resistance, which may be caused by a variation of the concentration of electrically active centers of one type and, therefore, by a variation of the compensation degree.

A compound $Cd_xZn_{1-x}Te$ belongs to the well-known and promising solid solutions, which a remarkable number of works of different authors have been devoted to for recent decades. Many works reported the results of researches concerning intrinsic defects and external impurities, which made possible to fabricate $Cd_xZn_{1-x}Te$ specimens with a high specific resistance (of the order of 10^9 Ω cm).

It is known that hydrogen in semiconductors is a passivating factor for many kinds of defects and impurities. In particular, it neutralizes shallow- and deep-level charged impurities and defects [1–3], which promotes an opportunity to produce semiconducting materials with a uniform concentration of impurity-defect centers. In the course of studying the passivation, hydrogen has been discovered to form complex molecules with impurity atoms [1].

There are some works dealing with the passivation (see, e.g., [4, 5]), which have reported the passivation of defects in CdTe, in particular, the passivation of shallow-level acceptor centers in specimens with p-conductivity. Their treatment with hydrogen has resulted in the total disappearance of the exciton peak owing to the passivation of a residual acceptor or/and to a reduction of the intensity of the peak that was connected with shallow-level impurities [6, 7]. Deep levels in CdTe and ZnTe were not engaged. However, hydrogen can passivate deep levels in CdZnTe and CdHgTe [1, 8]. The hydrogen-stimulated passivation of defects and impurities in $Cd_xZn_{1-x}Te$ has not been studied enough. This is connected, first of all, with the difficulties of introducing hydrogen into those materials.

Semiconductors $Cd_xZn_{1-x}Te$, even those synthesized from components of high-grade purity, are unsuitable for manufacturing the highly sensible detectors of electromagnetic radiation because of their low specific resistance. Their specific resistance at a temperature of 300 K is of the order of 10^6 Ω cm, whereas for manufacturing the mentioned semiconducting devices, $Cd_xZn_{1-x}Te$ with a specific resistance of more than 10^8 Ω cm is needed.

We grew $Cd_xZn_{1-x}Te$ crystals using the method of sublimation which allowed us to obtain substances that were quasi-homogeneous by composition. The grown ingots possessed conductivity of the p type and the hole concentration of no more than $10^9 - 10^{13}$ cm^{-3} at 300 K. The specific resistances of the specimens that had been cut off from various parts of the ingot differed to some extent, although deviations of the composition were insignificant.

The main attention has been paid to $Cd_xZn_{1-x}Te$ specimens with $x = 0.9$ and 0.6, where the passivation effect was appreciable.

Hydrogen was made diffuse into specimens either by warming up the latter in a hydrogen atmosphere at a temperature of 300 − 400 °C or from a gas discharge. In the latter case, specimens were placed in a leadaway pipeline at a distance of 6 cm from a discharge current.

1. Experimental Results

The influence of hydrogen on the impurity and defect distributions in various $Cd_xZn_{1-x}Te$ specimens reveals itself differently.

Fig. 1 presents the most characteristic temperature dependences of the electroconductivity of $Cd_{0.6}Zn_{0.4}Te$ specimens of the p type with high concentrations of acceptor centers (curves *1* and *2*). The hole concentration at 300 K was about 2×10^{12} cm^{-3}. The same figure shows the dependence $\sigma = f(T)$ of this specimen after its warming up at 400 °C for 160 h (curve

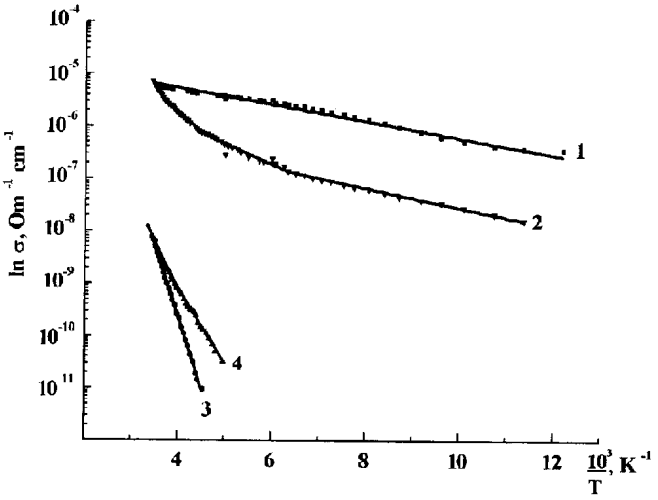

Fig. 1. Temperature dependences of the electroconductivity of $Cd_{0.4}Zn_{0.4}Te$ crystalline specimens: initial (*1* and *2*), warmed up in hydrogen at 400°C for 160 h (*3*), and after the diffusion of hydrogen in a gas discharge for 20 min (*4*)

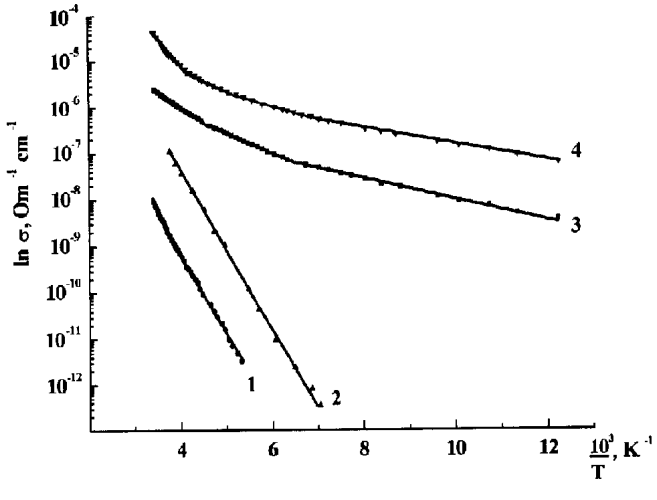

Fig. 2. The same as in Fig. 1 but for $Cd_{0.9}Zn_{0.1}Te$ crystalline specimens

3). One can see that the conductivity of this specimen reduced by almost three orders of magnitude at 300 K. In general, after warming up these specimens in a hydrogen atmosphere under the specified conditions, their conductivity changed by several to 10^4 times.

Similar variations of electric properties of the specimens with the *p*-type conductivity and a low specific resistance were also obtained when hydrogen diffused into $Cd_{0.6}Zn_{0.4}Te$ crystals from a gas discharge (Fig. 1, curve *4*).

However, the conductivity of high-resistance specimens after the introducion of hydrogen into them behaved quite differently. In Fig. 2, a dependence $\sigma = f(T)$ typical of such high-resistance $Cd_xZn_{1-x}Te$ specimens is displayed. Those crystals manifested similar dependences irrespective of the method how hydrogen had been introduced into them, either from a gas discharge or by warming the specimens in an H_2 atmosphere.

2. Discussion of Results

The researches carried out showed that the influence of hydrogen on electric properties of various $Cd_xZn_{1-x}Te$ specimens is different. In this connection, the researched specimens can be divided into two groups, namely, specimens with one and two types of impurity-defect centers. Specimens with the *p* type of conductivity and the initial specific resistance of $10^4 - 10^6$ Ω cm can be classified to the first group, while compensated insulating specimens with the specific resistance of about 10^8 Ω cm at 300 K to the second one.

An abrupt growth of the specific resistance was observed in the specimens of the first group after the introduction of hydrogen into them. A contribution of the shallow-level acceptor centers with the energy of activation of about 0.05 eV, which were situated in unwarmed regions, to the total specific conductivity of those specimens decreased substantially. Deeper levels with a deposition energy of 0.28, 0.39, and 0.55 eV (depending on the specimen) reckoned from the top of the valence band appeared instead. After warming up the specimens of this type in vacuum at 400°C, the growth of the resistance was not observed. So, one can assume that the increase of the specific resistance in $Cd_xZn_{1-x}Te$ specimens, which had been warmed up in hydrogen under the same conditions, was stimulated, first of all, by the passivation of shallow-level electrically active centers which took part in conductivity.

The passivation of acceptor and donor centers in Ge, Si, GaAs, and InP substances was studied best. It was interpreted in the framework of two models: the saturation of broken bonds by hydrogen and the hydrogen-assisted formation of complicated neutral complexes [9–11]. In so doing, hydrogen, capturing a hole and interacting with an ionized acceptor electrostatically, forms a neutral complex. The process can be presented as

$$A^- + H^\circ + h = Z^\circ, \qquad (1)$$

where A^-, H°, h, and Z° are the concentrations of ionized acceptors, neutral hydrogen atoms, holes,

and neutral complexes, respectively. The degree of passivation depends on the concentrations of acceptor centers and penetrated hydrogen, as well as on temperature. Such complexes can exist under equilibrium conditions only at a temperature that is higher than the acceptor ionization temperature.

The influence of hydrogen on electric properties of semiinsulating $Cd_xZn_{1-x}Te$ crystals is more complicated. The specific resistance of such specimens, after the latter having been treated with hydrogen, mainly decreases. As is known, semiinsulating crystals with a specific resistance of about 10^8 Ω cm are compensated, as a rule. Therefore, they contain two types of impurities which are ionized even at low temperatures. So, ionized acceptors or donors and hydrogen can participate in the formation of a complex in this case. In this case, an electrically inactive complex and an impurity center (a donor or an acceptor) are to be formed with the participation of hydrogen; with the impurity center being able to take part in the conductivity at low temperatures as an independent impurity.

Among the investigated $Cd_xZn_{1-x}Te$ specimens, there were also such that changed their type of conductivity from the hole type to the electron one after hydrogen having been introduced into them. In such a case, it would be natural if the electroconductivity of semiinsulating $Cd_xZn_{1-x}Te$ specimens will grow, which was proved experimentally to be true in most cases (Fig. 2.).

Nevertheless, one cannot assert that the variation of electric properties in high-resistance compensated $Cd_xZn_{1-x}Te$ specimens occurs owing to the passivation phenomenon. Relation (1) is not always satisfied for those specimens in practice. Moreover, a reconstruction of the defect-impurity spectrum of high-resistance specimens occurs already at a warming temperature of 200°C, and, therefore, the concentration of shallow-level defect-impurity centers grows, as a rule. There is also no confidence that hydrogen does not stimulate the appearance of new defects in $Cd_xZn_{1-x}Te$ crystals, in particular, due to a probable hydrogen-stimulated decrease of the energy of formation of vacancies in a metal sublattice.

However, it is possible to draw a conclusion from the presented experimental data that the passivation phenomenon can be realized in some $Cd_xZn_{1-x}Te$ crystals; first of all, in specimens with one type of defects and impurities, in particular, those of the acceptor type.

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ПРО ПАСИВАЦІЮ ВОДНЕМ ЕЛЕКТРИЧНО АКТИВНИХ ЦЕНТРІВ В $Cd_xZn_{1-x}Te$

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Р е з ю м е

Проведено дослідження впливу водню на електричні властивості кристалів $Cd_xZn_{1-x}Te$ з кількома значеннями x. Показано, що в кристалах p-типу провідності водень пасивує мілкі акцепторні центри, що в низькоомних кристалах може привести до збільшення питомого опору від декількох до 10^3 разів. У високоомних компенсованих кристалах проникливий водень приводить до істотного зменшення їх питомого опору, що, можливо, зумовлено зміною концентрації одного типу електрично активних центрів, а отже, і ступеня компенсації.