INVESTIGATION OF PHOTOLUMINESCENCE AND ELECTROCONDUCTIVITY OF ZnTe GROWN IN HYDROGEN ATMOSPHERE

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We have investigated the low-temperature photoluminescence (PL) and the temperature dependence of the electroconductivity for ZnTe monocrystals grown in hydrogen atmosphere at various pressures. The increase in the hydrogen pressure in the range 0.4–3.0 Torr results in a rise of the intensity of exciton PL lines in the crystals grown at a pressure of 0.6 Torr; afterwards, one observes a tendency to its reduction, which is associated with the hydrogen passivation of fine acceptor centers in the given crystals. In ZnTe samples containing oxygen, there appear a wide radiation band in the energy range 1.7—2.0 eV and a narrow line with the radiation maximum located at 2.030 eV. It is supposed that these lines are associated with the radiation of a O_{Te}–A complex formed due to the substitution of tellurium with oxygen. An isovalent O_{Te} impurity results in the compressive deformation and the strong electron-phonon interaction, which forms a complicated radiation spectrum with the participation of LO (25.3 meV), LA (14.5 meV), and TA (7.4 meV) phonons.

1. Introduction

Zinc telluride belongs to semiconductors whose properties are now intensively studied despite the long-term history of their investigation. Due to the large width of its forbidden band (2.28 eV at 300 K), ZnTe is considered to be a perspective material in optoelectronics. On its basis, one manufactures high-speed optical switches, detectors of ionizing radiation, low-dimension structures with Schottky barriers, etc.

In view of the wide practical use of ZnTe, the special attention is paid to the investigation of its electrical and optical properties. As the parameters of photoelectric characteristics essentially depend on the composition of crystals, the concentration and charge state of defects, and the uniformity of their distribution, the primary task lies in the improvement of the growing technology of semiconductor materials.

ZnTe has a high fusion temperature (1239 °C), that's why the much attention is paid to the methods which give a possibility to grow crystals at a temperature lower than the fusion one.

In the majority of investigations, one uses ZnTe crystals grown by means of the method of chemical transport reactions [1,2], the method of free growth from the vapor phase in dynamic vacuum [3], in liquid tellurium by the vapor–liquid–crystal mechanism [4], etc.

The given paper is devoted to the investigation of the electroconductivity and low-temperature PL of ZnTe single crystals grown in hydrogen atmosphere.

2. Experimental Results and Their Discussion

In semiconductors, hydrogen has particular properties: it passivates some impurity-defect centers making them electrically inactive. Under such conditions, one can increase the specific resistance of semiconductors, the lifetime of charge carriers, their mobility, etc. With the help of the passivation of electrically active centers and the filling of breaking bonds, it is possible to approach the properties of surface layers of semiconductors to those of volume ones. The passivation of structurally defect centers is most extensively studied in Si, Ge, and $A^{III}B^{V}$, as well as in other semiconductors.

The influence of hydrogen on the electrophysical properties of ZnTe isn't sufficiently studied yet, despite the appearance of some new works. In works [5,6], the low-temperature PL allowed one to discover the hydrogen passivation of, in the first turn, shallow acceptor centers. Forming complexes with some impurity-defect centers, hydrogen passivates them, that is, it makes them electrically inactive. It's worth noting that the passivation of impurity-defect centers with the help of hydrogen depends on many factors: a surface treatment of crystals, charges of impurities and defects, and temperature. At high temperatures, complexes

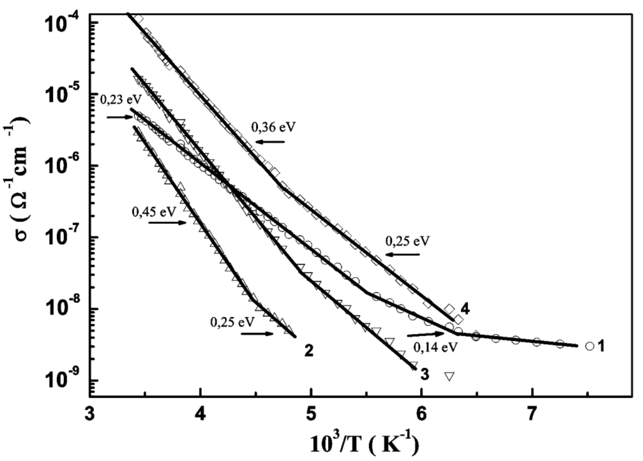

Fig. 1. Temperature dependence of the dark electroconductivity of ZnTe: *1* — initial sample; *2, 3, 4* — samples treated in a hydrogen gas discharge at T=300 K during 1 h

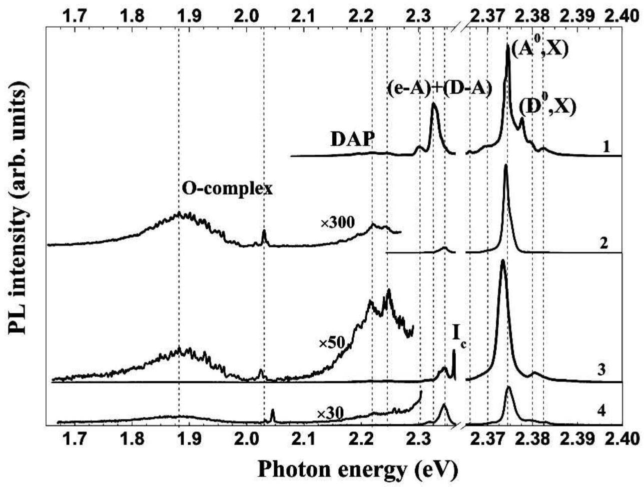

Fig. 2. Photoluminescence spectra at 5 K: *1* — ZnTe monocrystal grown in vacuum; *2, 3, 4* — ZnTe monocrystal grown in hydrogen atmosphere at p = 0.4, 0.6, and 3.0 Torr, correspondingly

created with the help of hydrogen usually either appear unstable or are not formed. For example, we managed rarely to passivate some impurities in ZnTe at a temperature of 400 °C, which was evidently associated with the excess of some limiting temperature of the formation of complexes. In most cases, hydrogen is introduced into crystals from a gas discharge. In this method, the hydrogen diffusion depth can reach several μm. That's why, in order to saturate the whole volume of the samples with hydrogen, we grew ZnTe crystals by the sublimation method at a temperature of 1075 °C in hydrogen atmosphere at various pressures (p=0; 0.4; 0.5; 0.6; 3.0 Torr), as well as in vacuum. The grown crystals were p-type of conductivity and the specific resistance of the order of 10^5 Ohm·cm at 300 K.

At this temperature of growth, hydrogen isn't involved into the formation of complexes, as the temperature of the formation and existence of complexes with its participation is lower. We didn't manage to determine its accurate value; in addition, it can be different for various defect structures of crystals. By means of growing ZnTe in hydrogen atmosphere, it was supposed to introduce hydrogen in the volume of a crystal, which would promote the formation of complexes, if the crystal is cooled after the crystallization to a temperature lower than that necessary for their existence.

Figure 1 shows the temperature dependence of the electroconductivity of the initial ZnTe sample (curve *1*). One can see that, in the investigated temperature range, there exist distinct levels with the energies of 0.24, 0.14, and 0.03 eV. After the one-hour treatment of the samples in a hydrogen gas discharge at a temperature of 300 K and a pressure of 0.25 Torr, the impurity-defect state of ZnTe is essentially changed (curves *2, 3* and *4*), i.e. there occurs their reconstruction. In the investigated temperature range, the samples treated in hydrogen now include the levels with energies of 0.36 and 0.28 eV. More rarely, there appears a level in the energy region of 0.41—0.45 eV (Fig. 1, curve *2*).

In Fig. 2, we present the PL spectra of the samples grown in vacuum (curve *1*) and in hydrogen at various pressures. Let's consider successively the spectra of PL lines of the samples grown in vacuum and in hydrogen. In the exciton region PL of the spectrum of the samples grown in vacuum, one observes the lines with the maxima at 2.3825 and 2.3794 eV. The former line corresponds to the free exciton (FE) emission. Based on works [4,7], the line with the radiation maximum at 2.3794 eV can be associated with the radiation of an exciton bound with a neutral donor (D^0X^*). As one can see from Fig. 2 (curves *2*, *14*), these lines with a lower intensity of radiation are also observed in ZnTe grown in hydrogen atmosphere.

The clearest line that corresponds to an exciton bound to acceptor (A^0X) has a doublet structure with the most intense peak located at 2.3745 eV and the less intense one — at 2.3735 eV. The former which is practically always present in ZnTe corresponds to the radiation with the participation of Li and Cu, while the latter can be possibly associated with the presence of Ag

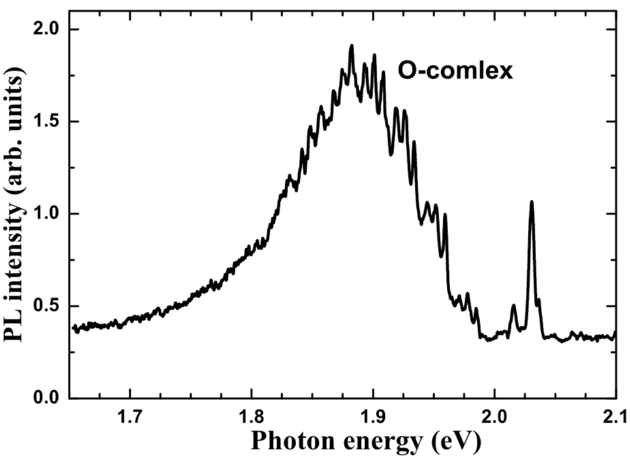

Fig. 3. Photoluminescence spectrum of ZnTe with oxygen impurity in the region 1.7—2.1 eV

impurities [4,7]. In ZnTe grown in hydrogen, only one peak of the line (A^0X) is observed, and its intensity essentially depends on the hydrogen pressure. These are 2.3741÷2.3747-eV lines (Fig. 2, curves *2, 4*) and a 2.3732-eV one (Fig. 2, curve *3*).

As one can see from Fig. 2, with increase in the hydrogen pressure up to 0.6 Torr, the intensity of the (A^0X) radiation lines first rises and then decreases. This dependence is conditioned by the relationship between the concentration of structural impurity centers in the crystal and the hydrogen concentration in its volume. As hydrogen passivates acceptor centers in ZnTe making them electrically inactive, the increase of the hydrogen pressure results in a decrease of the concentration of A^0-centers. The reduction of the concentration of acceptor centers following the introduction of hydrogen into the crystal is confirmed by the data of investigating the electric properties of ZnTe crystals treated in a hydrogen gas discharge and given in Fig. 1. That is, in the given case, the phenomenon of passivation of acceptors plays an important role in the formation of the radiation intensity of the (A^0X) lines. In the long-wave part of the (A^0X) lines of the crystal grown in vacuum, there appear lines with the maxima at 2.3694, 2.3660, and 2.3570 eV.

The 2.3570-eV line replica a phonon replica of the lower polariton branch of an exciton. It also manifests itself in the samples grown in hydrogen atmosphere. The 2.3660- and 2.394-eV emission lines can be possibly associated with the radiation of the complexes based on Zn vacancies of various charges.

In the near-band edge region PL of the samples grown in vacuum, one mainly observes a wide band (e—A)+(D—A) and its phonon replicas. The decomposition of this band into Gauss lines indicates the presence of an acceptor with an activation energy of 50 meV and a donor with that of 8 meV. According to the data [5], the 50-meV level corresponds to the energy level of a Zn vacancy. The (e—A)+(D—A) band in the samples grown in hydrogen is shifted by 20 meV towards the short-wave region with respect to the same line in the samples grown in vacuum.

Figure 2 (curve *3*) clearly demonstrates the line with a radiation energy of 2.3611 eV and its phonon replicas. According to [4], this is the line of an exciton bound to double-charged acceptor, the so-called I_c line, that manifests itself together with D^+X. Under the assumption that the 2.3805-eV line represents the D^+X radiation peak, the high-intensity 2.3732-eV line can be associated with the radiation of a complex of the acceptor type based on V_{Zn}.

The peculiarity of PL of ZnTe grown in hydrogen is a wide band with the maximal intensity of radiation at 1.88 eV appearing in the impurity region in the energy range 1.7—2.0 eV (Fig. 3). Together with this band, one observes low-intensity lines with the radiation maxima located at 2.030 and 2.014 eV. The band with the maximal radiation at 1.88 eV is evidently conditioned by the oxygen impurity [4,5,7]. The 2.030- and 2.014-eV lines weren't discovered in the mentioned works, though the assumption about their possible existence was put forward. As one can see from Fig. 2, the oxygen band and these lines are interdependent. In the case of a higher intensity of radiation of the oxygen band, the intensity of the narrow line is lower and vice versa — with decrease in the intensity of the oxygen band, that of the given lines increases.

The energy position of the radiation centers of the 2.030-eV line is about 0.36 eV above top of the valence band. This level also appears in the temperature dependences of the electroconductivity of the samples stored in oxygen atmosphere at room temperature. The level at about 0.36 eV is most probably conditioned by the presence of oxygen in the samples. In ZnTe, oxygen represents an isovalent impurity and, when substituting tellurium whose tetrahedral radius is by a factor of 2.07 higher than that of O_{Te}, results in the formation of a local compressive deformation. On the one hand, this compressive deformation results in the appearance of an additional deformation-diffusion flow directed against the gradient-concentration diffusion in the system with of one kind defects (vacancies or impurity atoms), whose dimensions are less than those of matrix atoms. These regions of compression represent attractive centers for such defects, that is, oxygen binds with V_{Zn} by forming complexes, whose energy levels are shallower than those of the V_{Zn} vacancy itself [8].

This fact is confirmed by the PL spectrum in the neighborhood of 1.88 eV which is associated with the radiation of excitons bound to defects involving O_{Te}, as well as its wide spectrum conditioned by the strong electron-phonon interaction [9]. One observes a radiation spectrum that consists of LO, LA, and TA phonons with energies of 25.3, 14.5, and 7.4 meV, correspondingly.

Thus, in the spectrum of low-temperature PL of ZnTe grown in hydrogen at pressure of 0.4—3.0 Torr, no distinct lines that could be conditioned by the introduction of hydrogen atoms into ZnTe were observed. Analyzing the PL spectra for ZnTe crystals grown in vacuum and in hydrogen and the electric properties of ZnTe treated in a hydrogen gas discharge, one can conclude that, in ZnTe, hydrogen mostly passivates shallow acceptor centers. This becomes especially clear from the temperature dependences of the electroconductivity and the dependence of the edge PL on the hydrogen pressure.

The wide PL band in the long-wave region of the spectrum is associated with the fact that the investigated crystals include oxygen that represents an isovalent impurity in ZnTe. Its isovalent properties manifest themselves in the complicated radiation spectrum of LO, LA, and TA phonons.

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ДОСЛІДЖЕННЯ ФОТОЛЮМІНЕСЦЕНЦІЇ І ЕЛЕКТРОПРОВІДНОСТІ ZnTe, ВИРОЩЕНОГО В АТМОСФЕРІ ВОДНЮ

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Р е з ю м е

Проведено дослідження низькотемпературної фотолюмінесценції (ФЛ) і температурної залежності електропровідності монокристалів ZnTe, вирощених в атмосфері водню при різному тиску. Із збільшенням тиску водню в межах 0,4–3,0 мм рт.ст. інтенсивність екситонних ліній ФЛ в кристалах, вирощених під тиском до 0,6 мм рт. ст., зростає, після цього проявляється тенденція до її зменшення, що пов'язано з пасивацією воднем мілких акцепторних центрів в даних кристалах. В зразках ZnTe, в яких присутній кисень, проявляється широка смуга випромінювання в інтервалі енергій 1,7—2,0 еВ і вузька лінія з максимумом випромінювання 2,030 еВ. Припускається, що ці смуги пов'язані з випромінюванням комплексу O_{Te}-A, який утворюється шляхом заміщення киснем телуру. Ізоелектронна домішка O_{Te} спричинює деформацію стиску і сильну електрон-фононну взаємодію, що й відображує складний спектр випромінювання, в якому наявні коливання LO (25,3 меВ), LA(14,5 меВ) та TA (7,4 меВ).