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Hydrogen-related photoluminescence in CdTe

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Abstract

Nominally undoped CdTe was exposed to a hydrogen plasma at 160°C. After this treatment, seven typical photoluminescence lines are observed in the excitonic region. By implantation with low-energy H^+ all seven lines are also observed. They are assigned to the presence of hydrogen in CdTe. Substituting deuterium for hydrogen, the isotope shifts of these lines were investigated. Within the experimental resolution of 0.05 meV no isotope shifts are visible. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The passivation of both donors and acceptors by pairing with hydrogen has been proposed as a mechanism that limits the carrier concentrations in both n- and p-type CdTe [1–3]. Svob et al. annealed n-type CdTe : In in H_2 at 500°C [2], and Gurumurthy et al. treated CdTe : In in a hydrogen plasma at 150°C [4]. Both authors observed a reduction of the carrier concentrations after hydrogenation, which was explained by the formation of close In–H pairs. Annealing CdTe : Cl in D_2, however, hardly reduced the carrier concentration [5]. For p-type CdTe, more element-specific information has been obtained. CdTe : N was hydrogenated during photoassisted growth via molecular-beam epitaxy by Zhonghai et al. [6] and by annealing in H_2 at 350°C by Boudoukha et al. [1]. They report that the N-related photoluminescence lines were either not visible or disappeared, respectively. The disappearance of excitonic PL-lines, bound to Cu- and Ag-acceptors, was reported by Svob et al. [7] to occur after 150 keV H^+ implantation. In As- and N-doped CdTe, local vibrational modes were detected by infrared spectroscopy that were assigned to As–H [8–10] and N–H complexes [6], respectively.

The appearance of seven new photoluminescence (PL) lines labelled H_1–H_7 in the excitonic region of CdTe that was exposed to a hydrogen plasma has

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been reported and assigned to the presence of hydrogen in CdTe [11]. Whereas after low energy H^+ implantation only three of these lines were observed, all seven lines are now visible after implantation at 90°C. The present experiments confirm the assignment of the PL lines to the presence of hydrogen in CdTe. In addition, the isotope shifts of the seven lines after substitution of hydrogen by deuterium are investigated.

2. Experimental procedure

Nominally undoped, Bridgman-grown CdTe crystals were etched in a solution of 3% bromine in methanol for 30 s and rinsed in methanol to remove traces of bromine. In order to remove a tellurium film left during etching, the samples were treated in a solution of 1 N KOH in methanol for 6 min. In a last step, the samples were rinsed in methanol in an ultrasonic bath, in bi-distilled water, and, finally, in acetone. Hydrogenation was carried out by exposure of the samples to a hydrogen plasma at 160°C and 0.7 mbar for 1 h. During this treatment, the samples were placed 5 cm downstream of the glow discharge region, which was inductively excited by a radio frequency field. In addition, CdTe crystals, heated to 90°C, were implanted with 3×10^{14} cm^{-2} H^+ ions at 200 eV. The PL experiments were carried out at 1.8 K, using a HeNe laser (10 mW focused). The luminescence was dispersed in a 0.5 m grating monochromator and detected by a cooled photomultiplier with a multialkali cathode (plasma experiments) or by a liquid-nitrogen-cooled CCD-detector (implantation experiments). Annealing was performed in a N_2 atmosphere for 1 h at 90°C.

3. Experimental results

The excitonic region of the PL spectrum of a CdTe sample after treatment in the hydrogen plasma is shown in Fig. 1a. It differs from the spectrum of a non-hydrogenated sample by seven new lines at 1.5750(2) eV, 1.5770(2) eV, 1.5803(2) eV, 1.5851(2) eV, 1.5857(2) eV, 1.5861(2) eV, and 1.5909(2) eV, which are marked H_1–H_7,

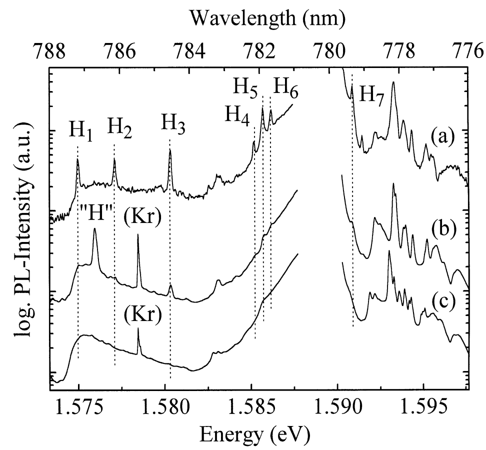

Fig. 1. (a) PL spectrum of a CdTe crystal treated in a hydrogen plasma at 160°C and 0.7 mbar for 1 h, compared with (b) the region of a CdTe crystal that was H^+ implanted at 90°C and (c) a non-implanted region of the same sample. The line labeled with “Kr” originates from a Kr calibration lamp measured simultaneously with the CdTe crystals.

respectively, in Fig. 1. The relationship of all the new lines, observed after the exposure to the hydrogen plasma, to the presence of hydrogen could be confirmed by implantation of CdTe with 200 eV H^+ at a temperature of 90°C. In earlier experiments, the lines H_1, H_2, and H_3 were not observed after implantation at 50°C, but after annealing at 90°C [11]. This seemed to indicate that hydrogen becomes mobile at about 90°C, and, therefore, the new implantations were performed at 90°C. All lines H_1–H_7 are observed in this case as is shown in Fig. 1b. To show the significance of the observed lines, the PL spectrum of a non-implanted region of the same sample is shown in Fig. 1c.

In addition to the lines H_1–H_7, a line appears at 1.5759 eV in Fig. 1b along with several satellites at the low-energy side, which are not clearly resolved. This characteristic line shape is very similar to a line at 1.5757 eV called the “H”-line that was observed after both 150 keV H^+ and 50 keV He^+ irradiation and was associated with irradiation-induced lattice defects by Svob et al. [7]. In the earlier experiments [11], the “H”-line appeared immediately after implantation at 50°C and disappeared after annealing for 30 min at 90°C. For this reason, the crystal implanted at 90°C was additionally annealed for 1 h at 90°C. The PL spectrum,

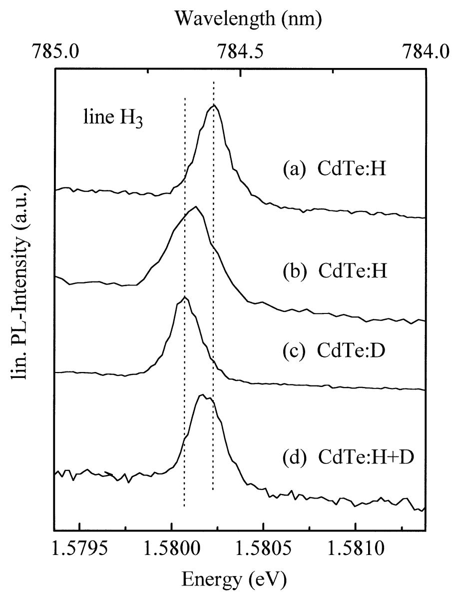

Fig. 2. PL spectra of CdTe crystals treated (a, b) in a hydrogen plasma, (c) in a deuterium plasma, and (d) in a plasma containing a 1 : 1 mixture of deuterium and hydrogen.

however, did not change significantly. The reason for the persistence of the "H"-line is not understood, up to now.

As is shown in Fig. 2a and Fig. 2b, the spectral positions of the observed lines vary within 3.5 meV for different samples treated in a hydrogen plasma. This shift occurs simultaneously for all excitonic lines including the acceptor- (A^0X) and donor-bound (D^0X) excitons. The positions of the A^0X and D^0X lines also vary in untreated samples. Therefore, it is concluded that the observed variations are not related to the plasma treatment. Rather, they seem to be caused by strain due to extended defects, like dislocations.

If hydrogen is a constituent of the defects causing the lines H_1–H_7, the substitution of hydrogen by deuterium might lead to an isotope shift [12], though this is not observed in many cases [13,14]. Fig. 2c shows that treating CdTe in a deuterium plasma produces the lines H_1–H_7 in the same spectral regions as the treatment in a hydrogen plasma. For this reason, a CdTe crystal was exposed to a plasma containing a 1 : 1 mixture of deuterium and hydrogen. Again, the same single lines are observed, and their half-widths are not larger compared to the treatment in a pure hydrogen or deuterium plasma (Fig. 2d). If any isotope shift exists, it does not exceed 0.05 meV for each of the seven lines.

4. Discussion

The appearance of the seven lines H_1–H_7 cannot be explained by radiation damage, because the kinetic energy of the hydrogen atoms in the plasma, accelerated by the radio frequency field, is comparable to thermal energies at 160°C. Furthermore, the lines are not caused by the heat treatment at 90°C during the implantation process or by the etching treatment, because the non-implanted region of the same sample does not show these lines. Since all lines are also observable after 200 eV H^+ implantation, they are caused neither by impurities, introduced by the plasma treatment, nor by intrinsic defects produced through the etching effect of the hydrogen plasma. For these reasons, the lines H_1–H_7 are assigned to the presence of hydrogen in CdTe. The non-existent or only very small isotope shifts of the lines do not contradict the fact that hydrogen is a part of the defects causing these lines, because isotope shifts of zero phonon lines are often very small [13,14].

From the small half-width (0.08 – 0.15 meV) and the spectral positions of the seven lines, it is concluded that they originate from the recombination of bound excitons. The relative intensities of the more thoroughly studied lines H_1, H_2, and H_3 vary for CdTe crystals from different batches. This behaviour might indicate that the lines originate from hydrogen associated with defects that are already present at different concentrations in the different batches.

The detection of the hydrogen lines by PL shows the incorporation of hydrogen into CdTe by a hydrogen plasma. This process has been discussed controversially in the literature [15,16,4]. To our knowledge, the lines H_1–H_7 have not been reported in hydrogen-doped CdTe before. But, it should be noted that Kozanecki et al. have implanted nominally undoped bulk CdTe with $5\times10^{15}\ cm^{-2}$ H_2^+ molecules at an energy of 30 keV per atom and annealed at 250°C for 5 min in a N_2 atmosphere [17]. Their PL spectra clearly exhibit two lines, which are not discussed in that paper but fit to the lines H_1 and H_3 in the present experiments.

In conclusion, the presence of hydrogen in bulk CdTe leads to seven PL lines in the excitonic region. As a consequence of technical importance, it is stated that the exposure of CdTe to a hydrogen plasma at 160°C leads to the introduction of hydrogen. Within the experimental resolution of 0.05 meV no isotope shifts are visible.

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