Hydrogen-related photoluminescence in CdTe

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CdTe, nominally undoped, was exposed to a hydrogen plasma and to low energy H^+ implantation. Under both conditions, seven typical photoluminescence lines are observed in the excitonic region. They are assigned to the presence of hydrogen in CdTe. © *1998 American Institute of Physics.* [S0003-6951(98)00105-3]

The passivation of both donors and acceptors by pairing them with hydrogen has been proposed as a mechanism that limits the carrier concentrations in both n- and p-type CdTe.[1,2] Although some results have been published in recent years,[3] information on the incorporation of hydrogen into CdTe remains scarce. 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 groups 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 (PL) lines were either not visible[6] or disappeared.[1] The disappearance of excitonic PL lines, bound to Cu and Ag acceptors, was reported by Svob and Marfaing[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 (Refs. 8–10) and N-H complexes,[6] respectively.

We report on PL experiments in nominally undoped, Bridgman-grown CdTe crystals. They 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 bidestilled 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 50 °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. Annealing was performed for 30 min in a N_2 atmosphere in the temperature range 60 °C–120 °C and in a Cd atmosphere in the temperature range 300 °C–330 °C.

Figure 1 shows the excitonic region of the PL spectrum of a CdTe sample after treatment in the hydrogen plasma. It is dominated by excitons bound to neutral acceptors (A^0X) at 1.5900 eV and to neutral donors (D^0X) at 1.5933 eV. It differs from the spectrum of a non-hydrogenated sample by seven new lines which are marked by H_1–H_7 in Fig. 1 and listed in Table I. In order to identify the processing step that is responsible for the occurrence of the new lines, a CdTe crystal was treated according to the following procedure (see Fig. 2):

(a) pre-annealing at 330 °C in a Cd atmosphere for 30 min, in order to avoid modification of the sample during the subsequent temperature treatments in steps (b) and (c);

(b) treatment in a hydrogen plasma at 160 °C for 1 h;

(c) annealing at 300 °C in a Cd atmosphere for 30 min.

The PL spectra recorded after each treatment are shown in Figs. 2(a)–2(c). The seven lines from Fig. 1 are observable again after step (b) and are absent after steps (a) and (c). This suggests that hydrogen is introduced into the samples during the plasma treatment and leaves the samples during annealing at 300 °C. It should be mentioned that after step (b) the intensities of the excitonic lines are reduced by a factor of about 10, while the intensities of the other PL signals are reduced by only a factor of about 4. This behavior

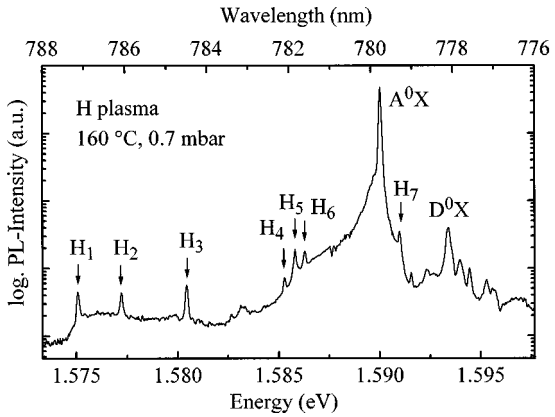

FIG. 1. PL spectrum of a CdTe crystal treated in a hydrogen plasma for 1 h.

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TABLE I. Energetic positions of the seven hydrogen-related PL lines, H_1–H_7, in CdTe along with their statistical errors (in parentheses).

Line	Position (eV)
H_1	1.5750(2)
H_2	1.5770(2)
H_3	1.5803(2)
H_4	1.5851(2)
H_5	1.5857(2)
H_6	1.5861(2)
H_7	1.5909(2)

would be expected for a reduced excitation intensity. Since the laser intensity was not varied, this behavior seems to be caused by non-radiative defects near the surface which were produced by the etching effect of the hydrogen plasma. The relative intensities among the excitonic lines do not change significantly. Therefore, it is concluded that no passivation of the associated donors or acceptors has taken place.

In order to investigate the relationship of the new lines to the presence of hydrogen, CdTe was implanted with 200 eV H^+. Immediately after implantation a line appears at 1.5760 eV along with several satellites at the low energy side, which are not clearly resolved [Fig. 2(d)]. This characteristic line shape is very similar to a line at 1.5757 eV that was observed after both 150 keV H^+ and 50 keV He^+ irradiation and was associated with irradiation-induced lattice defects by Svob and Marfaing.[7] Annealing at 60 °C does not change the PL spectrum, but after annealing at 90 °C this line disappears, and lines H_1, H_2, and H_3 are observed as is shown in Fig. 2(e). Annealing at 100 °C and at 110 °C does not change the PL spectrum. Annealing at 120 °C, however, removes lines H_1, H_2, and H_3 [Fig. 2(f)]. Lines H_4–H_7 are very weak after implantation and annealing at 90 °C and do not significantly rise above the noise level.

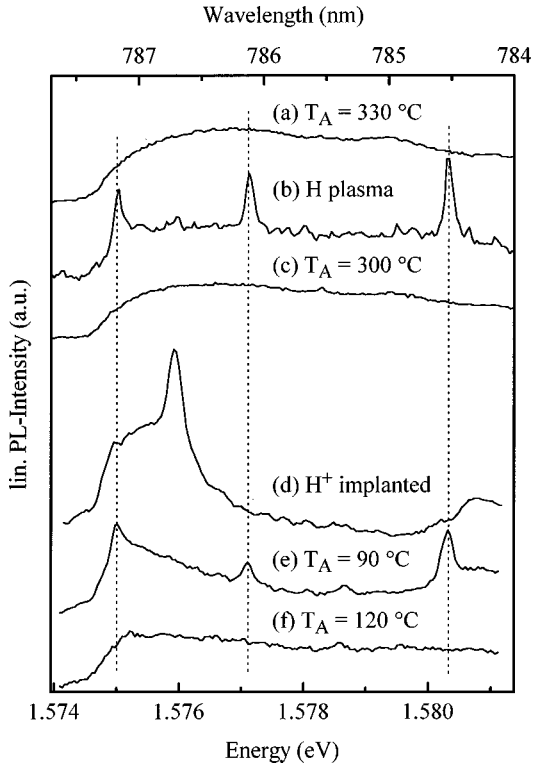

FIG. 2. PL spectra of a CdTe crystal that was (a) pre-annealed, (b) treated in a hydrogen plasma at 160 °C, and (c) subsequently annealed. For comparison, PL spectra of a CdTe crystal are shown that was (d) H^+ implanted at 50 °C, and (e) and (f) subsequently annealed at different temperatures.

The average depth of H^+ ions immediately after 200 eV implantation is only 6 nm. The H^+ ions, however, diffuse into the sample at 90 °C (annealing after implantation) or 160 °C (plasma treatment) with a penetration depth of at least some μm. This has been shown with C-V measurements after treatment of nominally undoped Bridgman-grown CdTe in a hydrogen plasma at 80 °C for 30 min by Kim *et al.*[11] Hence, PL investigates a completely hydrogenated layer, because the penetration depth of light at 633 nm is 0.5 μm,[12] and the diffusion length of electrons and holes is in the order of 1 μm.[13]

The appearance of the seven lines H_1–H_7, listed in Table I cannot be explained by the applied temperature of 160 °C used during the plasma treatment, because the sample has been exposed to a higher temperature of 330 °C before. Furthermore, the lines are not caused by irradiation 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. Since lines H_1, H_2, and H_3 are also observable after 200 eV H^+ implantation, they are neither caused by impurities introduced by the plasma treatment nor by intrinsic defects produced through the etching effect of the hydrogen plasma. Of course, it is possible that 200 eV implantation followed by annealing at 90 °C produces the same damage defects as the etching effect of the hydrogen plasma. But defects which are produced with such different methods and are stable at room temperature would probably frequently be observed in CdTe PL spectra. For these reasons, the three lines, H_1, H_2, and H_3, are assigned to the presence of hydrogen in CdTe. Since lines H_4–H_7 always appeared simultaneously with lines H_1, H_2, and H_3 after the treatment in a hydrogen plasma, lines H_4–H_7 are also concluded to be related to the presence of hydrogen in CdTe. Indeed, recent 200 eV H^+ implantations at temperatures above 50 °C produced these lines more strongly.[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 H_1, H_2, and H_3 lines vary for CdTe crystals from different batches. This behavior might indicate that the lines originate from hydrogen associated with defects that are already present at different concentrations in the different batches. The binding energies of hydrogen to these defects should be similar because all lines disappear within a temperature interval of 10 °C at the same annealing temperature [Fig. 2(f)]. The visibility of the hydrogen lines after plasma charging at 160 °C seems to point to an equilibrium situation between in- and outdiffusion of hydrogen which according to the implantation data should be mobile at 90 °C.

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.[4,11,15] To our knowledge, the H_1–H_7 lines have not been reported in hydrogen-doped CdTe before. But, it should be noted that Kozanecki *et al.* have implanted nominally un-

doped bulk CdTe with 5×10^{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.[16] Their PL spectra clearly exhibit two lines, which are not discussed in that paper but fit to the H_1 and H_3 lines in the present experiments.

In conclusion, both the exposure to a hydrogen plasma and low energy H^+ implantation lead to the same seven lines in the excitonic region of the PL spectra. The results obtained after low energy implantation are the strongest support for the interpretation that these lines are caused by the presence of hydrogen in bulk CdTe. As a consequence, it is stated that the exposure of CdTe to a hydrogen plasma at 160 °C leads to the introduction of hydrogen.

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