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Hydrogen vibrations in CdS

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The study of localized vibrational modes of hydrogen and deuterium in proton- and deuterium-implanted cadmium sulfide is reported. The observed SH and SD vibrations have energies of 2240 and 1775 cm^{-1}, respectively. A possible CdH vibration is observed at 1285 cm^{-1}, but the corresponding CdD mode falls in the region of multiphonon absorption and cannot be detected. The measured oscillator strengths for SH and SD modes are comparable with those reported for nonmetal hydrides in other II-VI compounds, whereas the integrated intensity of the CdH mode is smaller than for metal hydrides in other covalent semiconductors. This is probably because of weak CdH bonding and subsequent partial hydrogen release during bombardment or due to interaction with lattice phonons.

The possibility of passivating many point defects in a large variety of different semiconductors by introduction of atomic hydrogen has spurred new interest in this simple impurity and its bonding properties (for a recent review see the paper by Pearton *et al.*[1]). However, no general approach to hydrogen bonding in crystals has been developed so far. Given this situation an empirical approach is proposed, i.e., experimental determination of the hydrogen bond strengths measured through the energies of the localized vibrational hydrogen modes in various crystals. This paper continues our previous studies[2-4] of hydrogen vibrations in II-VI semiconductor compounds (CdTe, ZnTe, ZnSe). New compounds extend our tests of the simple models of hydrogen harmonic vibrations in crystals,[5,6] since the list of known hydrogen-related vibrations in semiconductors includes only ten materials. To help fill the gap we decided to study crystals of cadmium sulfide. This Brief Report presents new experimental results on the energy and oscillator strength of hydrogen vibrations in CdS, obtained by high-energy proton and deuteron implantation and subsequent infrared measurements.

For a discussion of the advantages of high-energy proton and deuteron implantations, as well as the description of the experimental technique used, the reader is referred to an earlier paper.[7] In the present experiment deuterons with maximum energy of 2 MeV were used. To obtain in CdS the same proton range of about 25 μm (see, e.g., Ref. 8) we lowered the implantation energy down to 1.65 MeV. We used very low proton or deuteron currents of 0.3 $\mu A/cm^2$; thus during 100 h of implantation we get doses of about 6.7×10^{17} $ions/cm^2$. Taking into account the range straggling for 1.65-MeV protons or 2-MeV deuterons in CdS of about 5 μm (Ref. 8) one obtains hydrogen-deuteron concentrations of roughly 2 at. % (or volume concentrations of about 1.35×10^{21} cm^{-3}). The crystals used for implantations were nominally pure. The circular samples with area of about 1 cm^2 were cut and mechanically polished on both sides to a thickness of about 1 mm. Before the implantation the samples were transparent to visible light and showed no metallic inclusions, thus demonstrating that the crystals used in this experiment were of good quality. After irradiation the implanted areas changed their hue from orange to brownish. This effect is due to the well-known near-edge band (NEB), which results from a high density of electronic states created in the band gap by the irradiation (see, e.g., Ref. 9). In the case of CdS this band is relatively weak [the NEB is also weak in ZnSe,[4] in contrast with very strong NEB in tellurium compounds: CdTe (Ref. 2) and ZnTe (Ref. 3)]. There seems to be a general rule that for the wider band gaps, NEB becomes weaker (see also our other papers on III-V compounds[10,11]). Our samples showed after implantation very strong interference fringes, from which we can calculate the maximal proton or deuteron ranges of about 25 μm. This result agrees well with the theoretical calculations based on the program of Ziegler *et al.*[8] However, strong interferences in the implanted layer exclude precise infrared measurements, necessary to establish hydrogen vibrational energies. In this situation we decided to polish our samples at the angle of about 0.1°, which nearly completely removed the fringes (see Figs. 1 and 2). The infrared measurements were done with a Nicolet MX-1 fast–Fourier-transform far-infrared spectrometer and an Oxford Instruments CF-100 cryostat. We have measured our spectra at room temperature as well as at near-liquid-helium temperature. To verify the experimental observation of hydrogen vibrations in a given crystal (as opposed to electronic transitions in radiation-induced defects) one can use the well-known isotopic effect due to the larger mass of deuterons, which results in a vibrational frequency lowered by a factor of $\sqrt{2}$. Experimental data for various implanted semiconducting crystals[10] show that due to anharmonicity of localized hydrogen-deuterium vibrations this factor usually has a smaller value, between

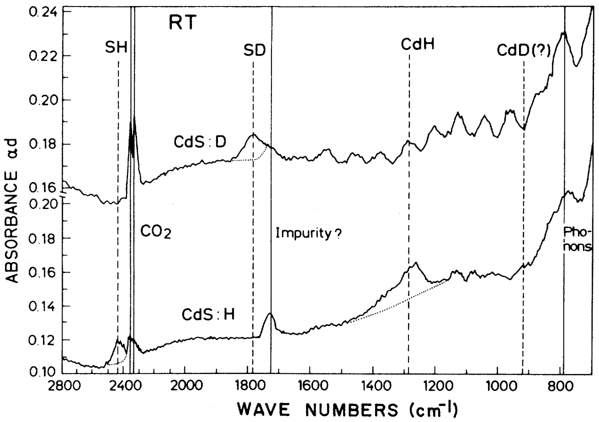

FIG. 1. Hydrogen- and deuterium-induced absorption bands in proton- and deuteron-implanted CdS, measured at room temperature.

TABLE I. Experimentally determined integrated absorptions A_0 and oscillator strengths f for hydrogen and deuterium localized vibrational modes in CdS. For details, see the text.

Material	Bond	ω_0 (cm^{-1})	A_0	f
CdS:H	SH	2440	4.3×10^{-4}	0.010
CdS:H	CdH	1285	2.2×10^{-3}	0.025
CdS:D	SD	1775	3.1×10^{-4}	0.010

1.395 and 1.375. As can be seen in Fig. 1, the bands at about 2440 cm^{-1} (for protons) and 1775 cm^{-1} (for deuterons) fit well into this scheme. We assign these high-energy vibrations to SH and SD molecules, respectively. Our models (see Refs. 5 and 6) predict for these molecules in CdS crystals vibrational energies of about 2400 and 1750 cm^{-1}, respectively. Similarly to hydrogen-deuterium-selenium bonds in zinc selenide (see Ref. 4) the presently observed bands have small intensity (see Table I) and thus small oscillator strengths of about 0.01 (about 20 times smaller than usually observed[10] for hydrogen vibrations in semiconductors). As pointed out in our earlier paper,[4] this can be easily explained by the assumption that only about 5% of all implanted hydrogens or deuterons are bonded with sulfur: our calculational procedure for the oscillator strength (see, e.g., Ref. 7) assumes that all implanted ions take part in the given vibration. Obviously in the case of semiconducting compounds this rule has to be changed: the total number of atoms taking part in different localized vibrations should be equal to the number of implanted ions. To calculate the oscillator strengths for the observed lines one uses the integrated absorption of localized vibrational modes. The energy-normalized integrated absorption A_0 is defined as

$$A_0=\int\frac{\alpha d}{\omega}d\omega\ , \tag{1}$$

where α is the additional, implantation-induced absorption coefficient, d is the thickness of the implanted layer, and ω is the energy of light. The oscillator strength f is then

$$f=2\times10^{15}\frac{A_0}{N}\omega_0 n\ , \tag{2}$$

where N is the ion dose/cm^2, n is the refractive index of the irradiated material (usually assumed to be equal to that of the crystalline one), and ω_0 is the mean energy of the localized vibrational mode. For deuteron implantations one uses a numerical constant of 4×10^{15}. The method of determination of f described above is very convenient,[7] since one does not need to know the thickness d of the implanted layer—instead, an ion dose per unit area is used in the calculations.

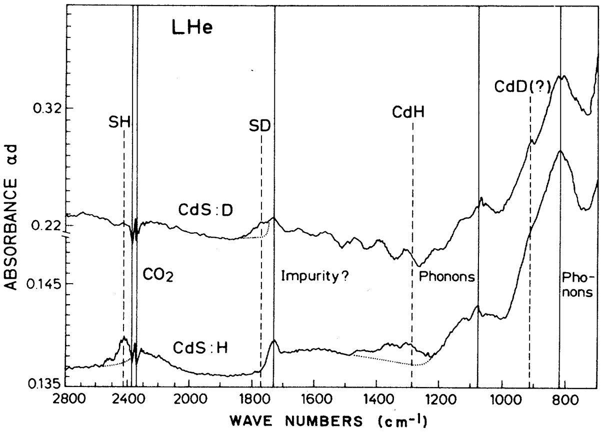

FIG. 2. Hydrogen- and deuterium-induced absorption bands in proton- and deuteron-implanted CdS, measured at liquid-helium temperature.

We have to address the question of group-VI-atom hydrogen bonds in other II-VI compounds already studied. Careful examination of our previous spectra of CdTe and ZnTe revealed very weak vibrations at about 1700 cm^{-1} which can be assigned to Te—H bonds. The weakness of these vibrations, as compared with those described above, stems from twice smaller dissociation energy of TeH molecules [about 48 kcal/mol (see Ref. 12)] as compared with SH molecules [about 81 kcal/mol (Ref. 12)]. Thus the probability of the formation of TeH molecules is much lower than the probability of SH bonding in the otherwise comparable crystals.

Similar problem of the weakness of the observed bands is encountered when we try to find CdH and CdD localized vibrational modes. We expect (see Ref. 5, where this prediction has been made) to find this mode around 1000±200 cm^{-1}. In fact (see Fig. 1) we observe a very broad band at about 1285 cm^{-1} which we ascribe to the CdH vibration. The corresponding CdD vibration should be seen around 900 cm^{-1}, which at room temperature falls in the region of multiphonon absorption. We tried to see the same band at about liquid-helium temperatures (Fig. 1). Although multiphonon absorption is then clearly smaller in the region around 1300 cm^{-1}, which permits unambiguous observation of CdH vibration, it is still strong around 900 cm^{-1}. Thus we are not able to confirm that the band around 1285 cm^{-1} is in fact the hydrogen vibrational mode of the CdH molecule, though this assumption seems quite plausible. The band (see Table I) shows a very small oscillator strength of about 0.025 [roughly 4 times smaller than the corresponding CdH band in CdTe (Ref. 2)]. This can be explained by partial release of hydrogen during irradiation (the on-beam annealing of the material) and also due to the very weak hydrogen-cadmium bonding (about 16.5 kcal/mol according to Ref. 13). Another possible explanation of the relative weakness of the observed localized vibrational modes of cadmium hydride is the interaction with the phonons in CdS and CdTe. This interaction can easily change the energy of the vibration as well as its intensity, due to the delocalization of the mode (for a discussion of these effects see Ref. 14), where a computer model has been employed to simulate the interactions of hydrogen localized vibrational modes with lattice phonons). The third possible explanation is that the charge transfer from cadmium to hydrogen is very small (small differences in electronegativities). Thus the effective charge, which in our calculational procedure has been assumed to be 1 [see Eq. (2) where no effective charge has been introduced], is also small and results in very small oscillator strengths.

In conclusion, we found new localized vibrational modes of hydrogen in CdS, which we ascribe to SH and CdH vibrations. The observed frequencies are similar to those already reported for other II-VI compounds and fit very well into the simple models of hydrogen vibrations in crystals.[5,6] The calculated oscillator strengths for the measured lines are very small, probably due to hydrogen release during irradiation or because of the weakness of cadmium-hydrogen bonds and the interaction with lattice phonons.

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