CH and CD Bond-Stretching Modes in the Luminescence of H- and D-Implanted SiC[†]

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H or D implantation of 6*H* SiC produces new luminescence spectra at 1.3°K. A striking difference between the H and D spectra are strong lines with energy displacements of 369 and 274 meV for H and D, respectively, energies that are recognized as those of the CH and CD bond-stretching modes. Annealing to 800°C increases the luminescence intensity, apparently by promoting the diffusion of H or D to a vacant Si site, where it forms a bond with one of the neighboring C atoms.

Localized vibrational modes in solids are usually due to the presence of light impurity atoms. H or D atoms may introduce very high-frequency modes. Examples are the *U* centers in alkali halides,[1,2] and OH^- in KCl.[3] We report the first observation of H- and D-induced modes in a covalent semiconductor. Implantation of H into SiC leads to the formation of luminescence centers having vibrational modes of 369 meV, more than three times the SiC lattice limit of 120.5 meV.[4]

Proton or deuteron implantation of SiC produces strong new low-temperature luminescence spectra. The maximum intensity is obtained by post-implantation annealing to about 800°C. A striking feature of the spectra are strong lines whose displacements from the no-phonon lines indicate the excitation of vibrational modes of 369 meV (2977 cm^{-1}) and 274 meV (2210 cm^{-1}) in H- and D-implanted samples, respectively. These energies are readily identified as the well-known CH and CD bond-stretching mode energies that are characteristic features in the spectra of organic molecules.[5,6]

Implanation displaces many lattice ions, leaving broken covalent bonds at the vacancies. In view of the annealing dependence, we propose that interstitial H or D diffuses to a vacant Si site and forms a bond with one of the four neighboring C atoms. Exciton recombination at such a center may then leave the CH or CD vibrational mode excited. No luminescence was observed that could be attributed to SiH or SiD centers, for which the bond-stretching frequencies are considerably lower.[7] The H or D luminescence was quenched by a 1200°C anneal, and the weaker preimplantation spectra were then restored.

Figure 1 shows the luminescence spectrum of a sample of 6*H* SiC implanted with 3×10^{14} H/cm^2 at 150 keV. The 6*H* polytype has three inequivalent Si or C sites,[8] hence there are three overlapping spectra, whose no-phonon lines are denoted by H_1, H_2, and H_3. In D-implanted samples the isotope shifts of the corresponding lines are only about 1 meV for D_1 and D_2, 2 meV for D_3. For convenience, a phonon energy scale has been included in Fig. 1. Because the H_3 spectrum is the strongest, the H_3 no-phonon line was chosen as the origin. Lattice phonon energies, with a limit at 120.5 meV, are shown by the dark strip with a gap between acoustical and optical branches

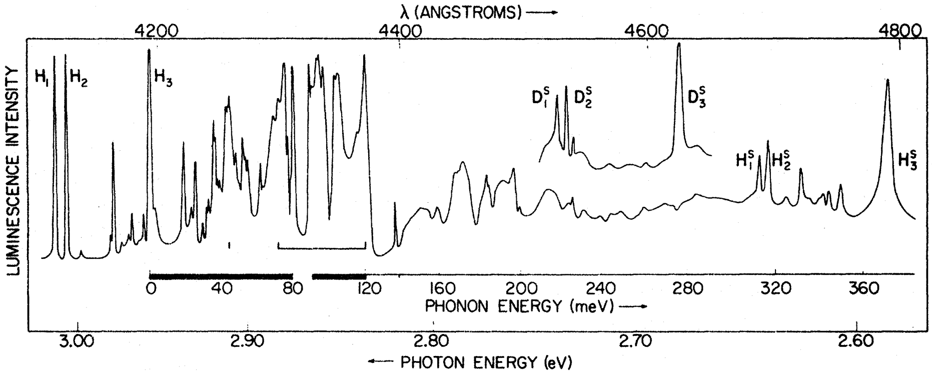

FIG. 1. Photoluminescence spectrum of H-implanted 6*H* SiC at 1.3°K. Three inequivalent lattice sites result in three overlapping spectra whose no-phonon lines are marked H_1, H_2, and H_3. Energies of H_3 phonons may be read from the special phonon energy scale, $H_3{}^S$ being at 368.8 meV. The inset shows the bond-stretching mode lines in D-implanted 6*H* SiC.

TABLE I. Energies of CH and CD bond-stretching modes in 6*H* SiC, and their ratios. The similar energies in the chloroforms are included as a typical example of such vibrational modes in organic molecules.

Spectrum	CH (meV)	CD (meV)	CH/CD
H_1, D_1	370.4	274.5	1.3494
H_2, D_2	367.2	272.2	1.3490
H_3, D_3	369.0	273.6	1.3487
$CHCl_3$, $CDCl_3$	374.3 [a]	279.7 [a]	1.3382

[a] Ref. 11.

from 80 to 91 meV. The H_3 portion of the one-phonon spectrum consists of a line at 46 meV and all the lines between 73 and 120.5 meV, as indicated by markers above the scale. Beyond the 120.5-meV lattice limit are some two-phonon bands of H_1, H_2, and H_3, and finally the bond-stretching mode lines denoted by H_1^s, H_2^s, and H_3^s, with the latter at 369.0 meV on the H_3 phonon-energy scale.[9] The D spectrum is very much like the H spectrum except for the displacements of the CD stretching mode lines, which are shown in the inset as D_1^s, D_2^s, and D_3^s.[10]

In Table I we list the stretching-mode energies as measured in the three H spectra and in the three D spectra, and, for comparison, the similar energies reported for Raman scattering in the chloroforms, $CHCl_3$ and $CDCl_3$.[11] The measured CH/CD ratios are close to an approximate calculated ratio of 1.3628, obtained by considering only the reduced-mass differences in the CH and CD pairs. Note that the three CH/CD ratios in 6*H* SiC agree to about one part per thousand, although there are approximately 1% differences in the CH and CD energies at the three inequivalent sites, due perhaps to the small but measurable differences in nearest-neighbor distances.[12] The exciton energy gap[8] of 6*H* SiC is 3.023 eV, hence the exciton binding energies at the three *H* sites are 10, 17, and 67 meV. The large differences in these energies are probably due to the Kohn-Luttinger interference effect in the electron wave function,[13] for the conduction-band minima are at the zone edge.

No other significant phonon differences in the H and D spectra were found that could be attributed to the CH and CD *bond-bending* modes. A gap mode of 81 meV is present in the H, absent in the D spectrum. A strong LA lattice mode of 77 meV is found in both spectra, and perhaps some of its intensity is drawn into the gap by a localized mode that involves the very light H atom, whereas the corresponding mode with D is resonant with and not distinguishable from the LA lattice mode.

The space group of 6*H* SiC is $P6_3mc$ (C_{6v}^4), and the symmetry requires that of the four possible CH bonds at a Si vacancy, the bond directed along the *c* axis should be different from the three nonaxial bonds. Therefore, one should really expect to see six CH spectra. At higher luminescence temperatures we do find additional spectra that we attribute to the axial CH centers, whose ground-state transitions are apparently forbidden. These will be reported later. The spectra observed at 1.3°K and reported here are believed to be those of the nonaxial CH and CD centers.

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[9] Additional lines in this region are bombardment-induced lines that are independent of the implanted ion. See L. Patrick and W. J. Choyke, Phys. Rev. B 5, 3253 (1972).

[10] Lines corresponding to the doubly excited stretching mode are observed in D-implanted samples, with a displacement in energy of 9 meV, less than double the single excitation energy. Thus, the anharmonicity is very close to that shown for the CD molecule in Table 39 of G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950).

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