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Photoluminescence of H- and D-implanted 4*H* SiC†

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A new luminescence center in 4*H* SiC is efficient during the first minute of exposure to the uv exciting light at 4 °K, but soon fades out, only to be fully restored by a room-temperature anneal. The center is an H atom bonded to a C atom at a Si vacancy and is formed by H implantation followed by annealing. Two such centers are formed at two inequivalent 4*H* sites, and only one is quenched. The other remains as an efficient luminescence center, as do both corresponding centers in D-implanted 4*H* SiC. The quenching mechanism is thought to be a change in the charge state of the center, the luminescence being attributed to exciton recombination at a neutral center. A g value of 4 is derived from magneto-optic measurements of the exciton in the ground state, indicating that the electron and hole spins are parallel. The 4*H* luminescence spectrum is similar in many ways to the primary spectrum of H-implanted 6*H* SiC. The secondary spectrum found in polytype 6*H* is absent from 4*H*. A doublet structure due to the presence of axial and nonaxial centers is described.

I. INTRODUCTION

We have reported efficient low-temperature luminescence centers in H- and D-implanted 6*H* SiC.[1–3] Annealing studies and the observation of C-H and C-D bond-stretching vibrational modes of 370 and 274 meV, respectively, suggested a model for the center, namely, an H (or D) atom bonded to a C atom at a Si vacancy. A similar luminescence is found in polytype 4*H*, which has the same symmetry (space group $P6_3mc$) but a larger energy gap ($E_{Gx} = 3.265$ eV).[4] In 6*H* SiC there are two kinds of spectra, called primary and secondary, which are attributed to exciton recombination at two different charge states of the same center.[3,5] In 4*H* SiC we find only the primary spectrum, which has phonon structure characteristic of exciton recombination at a neutral center. Excitons are bound to the two crystallographically inequivalent centers with the large binding energies of 110 and 126 meV. Very strong site dependence of exciton binding has been observed in H- and D-implanted 6*H* and 15*R* polytypes,[2,6] but it has not been adequately explained.

Recent high-resolution measurements show each no-phonon line to be an axial-nonaxial doublet, as expected for a uniaxial crystal, the C-H-bond direction being axial in one, and nonaxial in three of the four possible sites within a Si vacancy. The H atom at a Si vacancy lies within a tetrahedral cage of four C atoms, but it lies near only one of them, for the C-H bond length of 1.12 Å is small compared with the C-Si distance of 1.89 Å.

The rapid quenching of only one of the two centers in H-implanted 4*H* SiC, and the absence of quenching in D-implanted 4*H* SiC indicates a strong site dependence that remains unexplained. However, quenching has now also been observed for some of the centers in H-implanted 6*H* SiC after prolonged and intense uv irradiation.[5]

The 4*H* luminescence spectrum, like that of 6*H*, has lines due to the emission of five kinds of phonons, viz., momentum-conserving, zone center, resonant, localized, and internal (the C-H bond). There are many similarities between 6*H* and 4*H* spectra but there are also significant differences, some of which may be due to the very strong exciton binding in 4*H* SiC.

II. EXPERIMENTAL

A. Procedures

Preliminary experiments showed that the luminescence intensity of H- or D-implanted 4*H* SiC was very much like that of polytype 6*H* in its dependence on implantation levels, annealing temperatures, and crystal quality. We therefore followed the sample preparation methods discussed in detail in Ref. 2. A typical preparation was an implantation of 10^{15} H/cm^2 at 150 keV, followed by a 15-min anneal at 900 °C. This yields an H-atom density of about 10^{19} cm^{-3}.

The exciting light was provided by a mercury lamp filtered to exclude wavelengths greater than 3100 Å. Thus, the luminescence is largely from the implanted surface layer of about 1 μm. The polytype was originally determined from transmission Laue patterns, but can now readily be determined by observation of the H or D luminescence. In fact, the luminescence method is preferable, for it emphasizes the 1-μm surface layer that may make only a very weak contribution to the Laue pattern. Frequently, two polytypes are observed in this layer, supporting the conjecture that a surface layer of different polytype from the bulk is a common occurrence. The reason, presumably, is that the rapid drop in temperature at the end of the furnace run may promote the deposition of a dif-

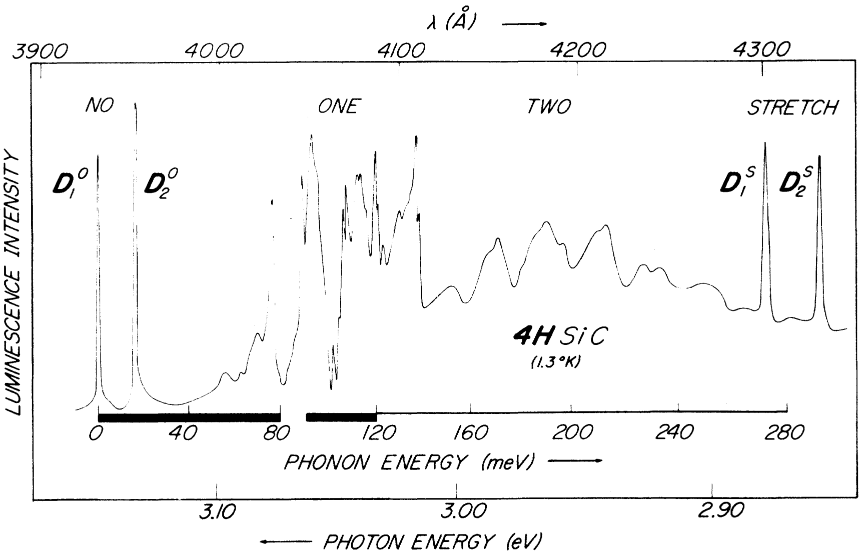

FIG. 1. Photoluminescence spectrum of D-implanted 4H SiC at 1.3 °K. There are two spectra, with no-phonon lines D_1^0 and D_2^0, and C-D bond-stretching mode lines D_1^s and D_2^s. There is considerable overlap of the two spectra in the indicated one-phonon and two-phonon regions. The phonon energy scale has its zero at D_1^0, and the darkened strip indicates the range of lattice mode energies, with a gap between acoustic and optic branches from 80 to 91 meV.

ferent polytype. On 4H crystals the most frequent alien surface layer is of the common polytype 6H.

The spectra were recorded photographically on Kodak 103 plates, and the portions shown here were copied from densitometer traces. Polaroid 57 film was used for exploratory work and for quenching experiments. The magneto-optic work was done at the Royal Radar Establishment in England.[7]

B. Results at 1.3 °K

Figure 1 shows the 1.3 °K luminescence spectrum of a sample implanted with 3×10^{15} D/cm^2, and annealed at 900 °C. D_1^0 and D_2^0 are no-phonon lines of the two crystallographically inequivalent deuterium centers, D_1 and D_2. Each line contains axial and nonaxial components, unresolved here. One-phonon and two-phonon regions of the two overlapping spectra are indicated, and, at the right, lines D_1^s and D_2^s that are due to photon emission in which the C-D bond-stretching mode is excited. As in the 6H spectrum, we could not find any lines due to the excitation of the C-D bond-*bending* modes.

The overlapping of the D_1 and D_2 spectra makes it difficult to observe the structure of the one-phonon spectrum. Fortunately, this problem does not exist for H-implanted samples because of the quenching that was mentioned earlier. Figure 2 shows a portion of the 1.3 °K luminescence spectrum of a sample implanted with 3×10^{14} H/cm^2. The no-phonon lines H_1^0 and H_2^0, are isotope shifted to energies 3 meV greater than the corresponding D lines. Note that H_2^0 is relatively weak.

Experiment showed that the strength of the H_2 spectrum was a function of the length of time that the sample had been exposed to the uv exciting light. H_1^0 and H_2^0 were of comparable intensity in a spectrum recorded with less than a minute of uv exposure. Figure 2 was recorded after a 10-min exposure. After an hour neither the axial nor the nonaxial component of the H_2 spectrum could be detected above the background noise. Mean-

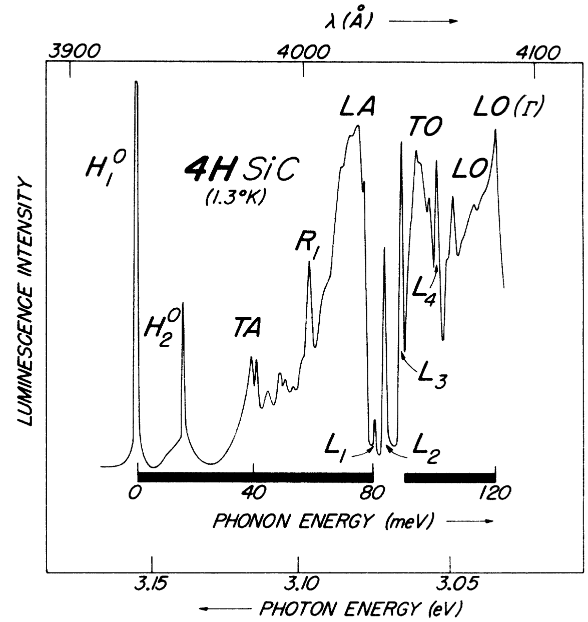

FIG. 2. Photoluminescence spectrum of H-implanted 4H SiC at 1.3 °K. Only the no-phonon and one-phonon regions are shown here. The phonon lines identified by letters all belong to the H_1 spectrum. The relatively weak line H_2^0 and its associated phonon lines are partially quenched by a 10-min exposure to the uv exciting light.

while, the H_1 spectrum showed no significant change in intensity. Thus, quenching occurs at only one of the two inequivalent sites, and only for the H center, i.e., *not* when D is substituted for H.

The H_2 spectrum could be completely quenched only at low temperatures. At 45 °K, H_2 became weak under exposure to the usual uv intensity, but it did not disappear. Regardless of the degree of quenching, a room-temperature anneal fully restored the spectrum; after cooling to 4 °K again, the H_1 and H_2 spectra were once more of comparable intensity during the first minute of exposure to uv. A partial restoration of H_2 could also be effected by irradiating for a few minutes with light of energy less than the band gap, i.e., light not capable of producing excitons.

In 6*H* SiC additional spin-forbidden lines are observed at 1.3 °K that give way to strong spin-allowed spectra at 4.2 °K.[2] These are called the secondary spectra,[8] and are now attributed to exciton recombination at a different charge state of the same center.[3] In 4*H* SiC we did not observe any additional lines at 1.3 or 4.2 °K, and we conclude that the comparable centers in 4*H* do not luminesce, presumably because they do not bind excitons.

The quenching of H_2 and the absence of secondary spectra allows us to examine the H_1 spectrum without the interference of any foreign lines. A comparison with a spectrum in which H_2 is *fully* quenched confirms that all the significant lines in Fig. 2 belong to H_1. The phonon scale, with origin at H_1^0, indicates the range of lattice phonon energies, with a gap between acoustic and optic branches from 80 to 91 meV, and a lattice limit of 120.5 meV.[9] The various phonon-emission lines are identified by letters in Fig. 2, and will be discussed in Sec. III.

The H_1^s and H_2^s lines of the C-H bond-stretching modes are off-scale in Fig. 2, but we list their energies in Table I, together with those of D_1^s and D_2^s shown in Fig. 1. A comparison with similar modes in 6*H* and 15*R* polytypes indicates that there is very little dependence of mode frequency on either site or polytype.

TABLE I. Energies of C-H and C-D bond-stretching modes and their ratios C-H/C-D for three polytypes. These modes are observed only in the primary spectra.

	Spectrum	C-H (meV)	C-D (meV)	C-H/C-D
4*H*	H_1, D_1	366.8	272.0	1.349
4*H*	H_2, D_2	370.1	274.5	1.348
6*H*	H_1, D_1	370.4	274.5	1.349
6*H*	H_2, D_2	367.2	272.2	1.349
6*H*	H_3, D_3	369.0	273.6	1.349
15*R*	H_1, D_1	366.8	272.0	1.349
15*R*	H_2, D_2	368.7	273.3	1.349

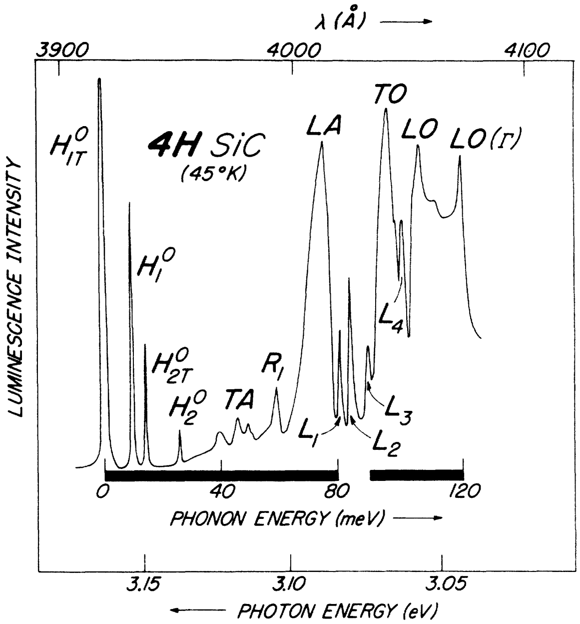

FIG. 3. Photoluminescence spectrum of H-implanted 4*H* SiC at 45 °K. All identified phonon lines belong to the thermally excited H_{1T} spectrum, which is dominant at this temperature. The H_2 and H_{2T} spectra are partially quenched.

C. Results at 45 °K

In H- and D-implanted 4*H* SiC, as in 6*H*, additional thermally excited spectra (with subscript T) are observed at higher temperatures. Because of the large 4*H* exciton binding energies, it is possible to record spectra up to about 60 °K, compared with about 30 °K in 6*H*. Figure 3 shows a 45 °K spectrum of the same sample used for Fig. 2. H_{2T} and H_2 are partially quenched, and the spectrum is dominated by H_{1T}, whose no-phonon line is the origin of the phonon energy scale. The reason that H_{1T} dominates is that the thermally excited states have oscillator strengths that are roughly 50 times greater than those of the ground states,[2] as previously observed in polytype 6*H*.

The schematic of Fig. 4 indicates the various exciton binding energies in both H- and D-implanted samples. A comparison with the similar figure for 6*H* SiC (Fig. 2 of Ref. 2) shows that the major differences are the much larger exciton binding energies for primary centers in 4*H*, and the complete absence of binding to secondary centers. The polarization directions of the no-phonon lines are also shown in Fig. 4. The previous discus-

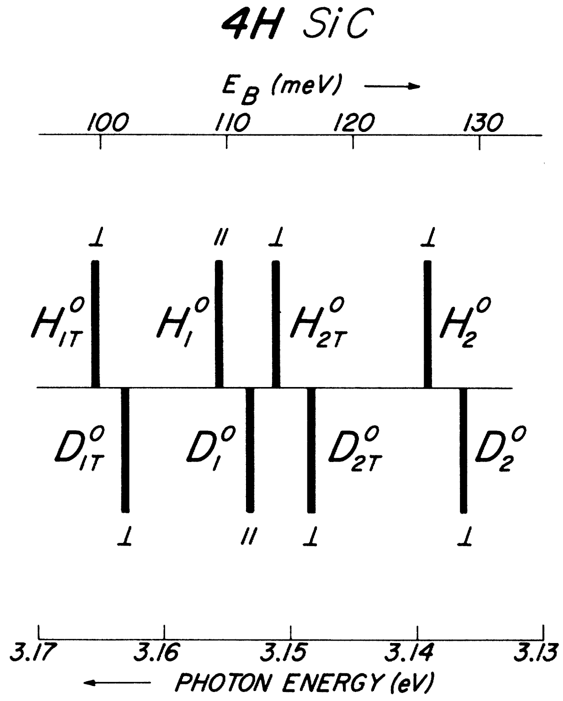

FIG. 4. Schematic drawing of all observed no-phonon lines in H- and D-implanted 4*H* SiC. The upper scale shows the exciton binding energy $E_B = E_{Gx} - h\nu$, with $E_{Gx} = 3.265$ eV. The displacements of the downward-pointing *D* lines from the corresponding upward-pointing *H* lines indicate the isotopic shifts of 2–3 meV. The polarization of corresponding lines is the same, as shown.

sion[2] of the strong site dependence of the polarization in 6*H* SiC is also valid for 4*H*.

There is a 4.8-meV thermally excited state in the spectrum of the neutral donor N in both 4*H* and 6*H* SiC, the excitation energy being independent of site and polytype.[2,4] In contrast, the thermal excitation energy in *H* and *D* centers is a function of both site and polytype. These energies are 9.9 meV for H_{1T} and 11.9 meV for H_{2T}.

D. Magneto-optic results

Extensive high-resolution magneto-optic measurements were made on both the primary and secondary spectra of polytype 6*H*.[5] Only a preliminary measurement was made on the H_1^0 line of 4*H* in a field of 34 kG to confirm its similarity to the three primary lines of 6*H*.

The high-resolution measurement showed that H_1^0 is an axial-nonaxial doublet with a separation of 0.48 meV between the two components. The measurement in the magnetic field showed that the exciton bound to H_1 has a *g* value of 4 ± 0.2 for $\vec{H} \perp \vec{c}$. No information was obtained on the H_2^0 line because of its quenching.

III. VIBRATIONAL MODES

This section is a review of the various phonon energies observed in the spectra of H- and D-implanted 4*H* SiC, emphasizing the many similarities with the 6*H* phonon spectrum, and a few differences. For this purpose we classify the phonons into five groups, as follows: (a) one C-H or C-D bond-stretching mode, (b) four localized (gap) modes, (c) one resonant mode, (d) two zone-center (Γ) modes, and (e) many momentum-conserving (MC) modes.

The bond-stretching mode (a) is the only one in which the substitution of D for H makes a substantial difference, as shown in Table I. The (b) and (c) modes have only slightly less energy in D-implanted samples, as shown in Table II. In the *H* spectra L_1, L_2, and L_3 fall in the gap between acoustic and optic branches. L_1 and L_2 probably overlap the LA peak in D-implanted samples, as L_1 does in 6*H* SiC. However, we were unable to resolve this structure, as we did in 6*H*, so the lines are shown as not observed (N.O.) in Table II. The L_4 mode may fall in a small gap between TO and LO branches. The R_1 resonant mode falls in a region where the lattice-mode density is small, and R_1 is not much broader than the *L* lines. The (b) and (c) modes are considered to be Si vacancy modes, and are similar to those observed in 6*H* SiC, although more modes are resolved and their energies are somewhat different.

The two other groups, (d) and (e), have the same energies in H- and D-implanted samples. The two (d) modes are TO(Γ) at 98.6 meV and LO(Γ) at 120 meV, in agreement with Raman measurements.[9] The (e) modes are quite broad in H- and D-implanted 4*H* SiC, probably because of the strong exciton binding. The MC modes were earlier measured in detail in the spectrum of the neutral donor, N, to which an exciton is weakly bound.[4] The narrow lines of Ref. 4 permitted us to identify 18 4*H* lattice modes. Both the polarization and the energy of an MC mode should be independent of the im-

TABLE II. Energies of resonant (*R*) and localized (*L*) modes in the spectra of 4*H* SiC samples implanted with H or D.

	H (meV)	D (meV)
R_1	59.0	58.1
L_1	80.5	*N.O.*
L_2	83.9	*N.O.*
L_3	89.6	89.3
L_4	100.9	100.4

purity center, and were found to be so in 6H SiC.[2] However, the 4H MC lines in Fig. 2 are too broad to make such a detailed comparison. Instead of 18 lines we have identified only the groups of lines TA, LA, TO, and LO.[10] We believe these observed MC bands are consistent with the previously observed 18 narrow lines when broadening is taken into account. Implications of the phonon spectrum were discussed at length for 6H SiC in Ref. 2, and the conclusions apply equally to 4H. In particular, the strong no-phonon and localized phonon lines imply strong localization of the exciton.

Although it is not shown here, the H_2 spectrum was recorded before quenching, and it was found to be very similar to that of H_1 in all its phonon structure. We could find no hint of anything unusual in H_2.

IV. MODEL OF LUMINESCENCE CENTER

We have shown that the low-temperature luminescence spectra of H- and D-implanted 4H SiC are very similar to the *primary* spectra of similarly implanted 6H SiC. We therefore adopt the luminescence-center model proposed for 6H SiC, i.e., an H or D atom bonded to a C atom at a Si vacancy. This model was supported by the extensive 6H annealing studies and by the heavy-ion bombardment of crystals grown in hydrogen.[2]

We find only primary spectra in 4H whereas in 6H we find both primary and secondary spectra, the two kinds of spectra having very different phonon structure and phonon to no-phonon ratios. The 6H primary and secondary spectra were incorrectly attributed to nonaxial and axial sites before the axial-nonaxial doublet structure was resolved.[2,3] They are now attributed, on the basis of their phonon structure, to neutral and to charged states, respectively, of the same luminescence centers. The 6H SiC magneto-optic measurements support this interpretation,[5] for they show that the exciton is strongly localized at the primary center but not at the secondary center. The short-range potential of a neutral center can be expected to localize the exciton[11] and thus give rise to the large spin (exchange) coupling that results in widely separated singlet and triplet spin states, as observed. On the other hand, the Coulomb potential of a charged center is less capable of localizing the exciton, which then responds to the magnetic field like an effective-mass exciton, as observed in the 6H secondary spectra.[5]

Because the 4H spectra are similar to the 6H primary spectra, we conclude that an exciton can be strongly bound to the neutral 4H center, but is not bound to the charged center. The failure of a charged center to bind an exciton is not uncommon and is apparently the reason for the absence of one of the three secondary spectra in 6H SiC. Often the charged center will bind *one* particle, say the electron, but the resulting neutral center is then unable to bind the hole.[12] The limited magneto-optic measurements in 4H SiC are consistent with the more extensive 6H measurements. In C_{3v} symmetry the ground-state splitting of H_1 with a g factor of four can be attributed to a Γ_3 exciton comprising the $M=\pm 1$ components of the $S=1$ triplet state.[13] The singlet state is then identified as the thermally excited H_{1T}, indicating an exchange splitting of 9.9 meV. The corresponding thermally excited state of the 6H SiC primary center was observed to be unsplit in a magnetic field.

The question of the number of charge states of the luminescence center has not been answered. For a Si vacancy in Si, three and possibly four charge states have been found in spin-resonance measurements,[14] but similar results are not available for SiC. Nevertheless, it seems plausible that different charge states in H-implanted SiC give rise to the two kinds of 6H spectra and to the quenching in both 6H and 4H. The restoration of the luminescence of the H_2 center by annealing is then attributed to the *release* of trapped charge, although the trapping mechanism has not been determined. Any explicit quenching model is confronted by the fact that only one of the two H centers is quenched, and neither of the D centers. Thus, the mechanism shows a suprising sensitivity to small site differences and to mass differences.

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[1] W. J. Choyke and Lyle Patrick, Phys. Rev. Lett. 29, 355 (1972).

[2] Lyle Patrick and W. J. Choyke, Phys. Rev. B 8, 1660 (1973).

[3] Lyle Patrick and W. J. Choyke, Phys. Rev. B 9, 1997 (1974).

[4] Lyle Patrick, W. J. Choyke, and D. R. Hamilton, Phys. Rev. 137, A1515 (1965).

[5] W. J. Choyke, Lyle Patrick, and P. J. Dean (unpublished).

[6] W. J. Choyke and Lyle Patrick, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors*, (PWN-Polish Scientific Publishers,

Warsaw, 1972), p. 177.

[7] We thank Dr. P. J. Dean of RRE for making these measurements possible.

[8] The primary spectrum was called nonaxial in Ref. 2, and the secondary spectrum was called axial.

[9] D. W. Feldman, J. H. Parker, Jr., W. J. Choyke, and Lyle Patrick Phys. Rev. 173, 787 (1968).

[10] This notation is convenient, but is based on cubic symmetry, and is therefore somewhat inaccurate for the 4*H* modes.

[11] D. G. Thomas, J. J. Hopfield, and C. J. Frosch, Phys. Rev. Lett. 15, 857 (1965); R. A. Faulkner, Phys. Rev. 175, 991 (1968).

[12] J. J. Hopfield, in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 725.

[13] A Γ_2 exciton comprising the $M = 0$ component has been identified in 6*H* SiC.

[14] J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Suppl. 7.