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Photoluminescence of Radiation Defects in Cubic SiC: Localized Modes and Jahn-Teller Effect*

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Radiation defects were introduced into cubic SiC by 120-keV He-ion implantation, or by 1-MeV electron bombardment. Some of the defects persist after a 1600 °C anneal. A low-temperature luminescence spectrum of one of the persistent defects reveals strong vibronic coupling, with localized and resonant modes. The spectrum has an unusual temperature dependence, with two abrupt changes below 13 °K. The changes are attributed to the Jahn-Teller effect, and the distortion is accounted for by coupling with the 66.5-meV resonant mode. A possible model for the defect is the Watkins-Corbett impurity-vacancy model that was found to be appropriate for several persistent defects in Si.

I. INTRODUCTION

Ion implantation shows promise as a technique for the fabrication of SiC devices.[1] It is important to anneal out lattice damage caused by the implantation. Hart *et al.*[2] used He backscattering to show that very little disorder remains after a 1200 °C anneal, but that a small amount persists to still higher temperatures. Low-temperature photoluminescence appears to be a useful tool for studying the persistent disorder.

We bombarded cubic SiC with 120-keV He^+ ions (10^{14} cm^{-2}) and subsequently annealed at 1300 °C. The 1.5 °K luminescence revealed a new vibronic spectrum with a number of resonant modes, and a strong localized mode in the gap between acoustic and optic branches. The spectrum was still observable but less intense after a 1600 °C anneal. The same luminescence center has also been introduced by electron irradiation; hence the He ions play no part in the luminescence.

In extensive work on electron-irradiated Si, Watkins and co-workers[3-5] have shown that the primary defects—vacancies and interstitials—are mobile at low temperatures, and are readily captured by impurities. Persistent defects are therefore likely to be impurity-defect complexes, and in the references cited[3] several have been identified as impurity-*vacancy* complexes. We expect that the distinction between the annealing temperature of primary and complex defects is also valid for SiC. Hence a luminescence center that is introduced by irradiation but survives a 1600 °C anneal is probably an impurity-defect complex. Our observation of Jahn-Teller effects in the spectrum reported here and a comparison with similar observations in Si suggest that the luminescence center may be an impurity-vacancy complex for which the Watkins-Corbett model is appropriate.[5,6]

The changes we attribute to the Jahn-Teller effect are observed as the luminescence temperature is increased. There are two abrupt changes in the spectrum between 1.3 and 13 °K. In each case the lower-temperature spectrum is extinguished as the higher-temperature spectrum is activated. Two of the spectra are tentatively attributed to the static and the dynamic Jahn-Teller configurations,[7] and the third to the undistorted center. The Jahn-Teller distortion appears to be due to coupling with the 66.5-meV resonant mode.

The high-temperature form of the spectrum has previously been observed by Geitsi *et al.*,[8] but with rather poor resolution.

II. EXPERIMENTAL PROCEDURE

A Van de Graaff accelerator was used for the electron bombardments (6×10^{17} cm^{-2} at 1 MeV), with the samples cooled at room temperature. An ion accelerator equipped with beam scanner and magnetic separator was used for the He^+-ion bombardments (10^{14} cm^{-2} at 120 keV), with samples at room temperature. All annealing at temperatures above 800 °C was done in an Ar atmosphere (15-min anneals).

The penetration of the He^+ ions was about 0.56 μm.[9] In exciting the luminescence, the penetration of the Hg light was kept to about the same distance by using filters to exclude wavelengths greater than 3100 Å. This reduced the background luminescence from the unbombarded crystal. The Dewars were fitted with fused-quartz windows.

The sample temperatures were known from He vapor-pressure measurements below 4.2 °K, the samples being immersed. At 77 °K the samples were immersed in liquid nitrogen. Between 4.2 and 77 °K the samples were not immersed in the refrigerant, and the actual temperature of the illuminated crystal was uncertain. Stated temperatures in this range are estimates.

The spectra were recorded on Kodak 103F plates. The data presented here were copied from densitometer traces. We did not make any correction of the intensities for the wavelength dependence of the spectrometer and the photographic plate.

III. LOW-TEMPERATURE SPECTRUM

An implanted ion may displace several thousand Si and C lattice atoms, producing gross damage that severely broadens any luminescence structure. The recovery of good structure requires an anneal of perhaps 1000 °C. Electron irradiation produces much less lattice damage, and good spectra are obtained without annealing. After electron bombardment at room temperature, many new and complex spectra are seen, with some sample to sample differences that indicate the importance of impurities. In our samples all the new spectra anneal out at various stages below 1300 °C except two that are also seen in He^+-bombarded samples after a 1300 °C anneal. We shall discuss one of these persistent spectra, shown in its low-temperature form in Fig. 1. It was observed in all of the more than ten samples examined.

Many of the properties of SiC to be investigated in ion implantation and annealing are expected to be largely independent of polytype. Cubic SiC, with the zinc-blende structure, has the advantage of simplicity for luminescence studies, for it has no nonequivalent Si or C lattice sites, and its symmetry and phonon structure are better understood. The energy gap is 2.39 eV.

The Brillouin zone has critical points at X, L, and W that give rise to maxima in the phonon density of states.[10] The energies of phonons at Γ, X, and L are known and are listed in Table I. The X phonon energies are measured in the indirect transitions of weakly bound excitons, for the conduction-band minima are at X.[11] The Γ phonons are observed in Raman scattering.[12] The L phonon energies are obtained indirectly from the Raman spectra of SiC polytypes by making the apparently good assumption that there is, for all polytypes, a common set of dispersion curves in the stacking direction.[12]

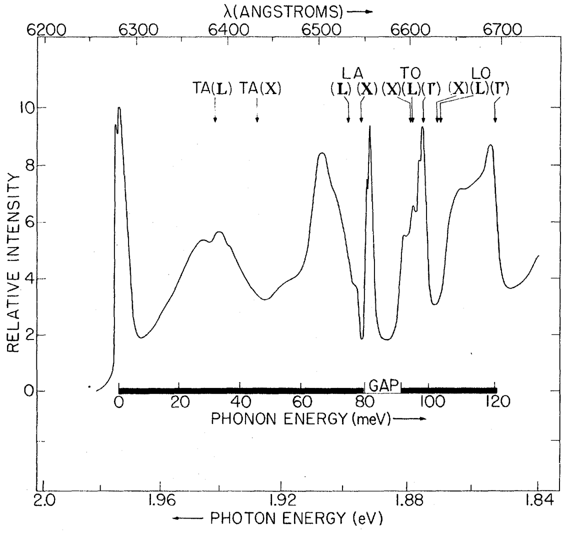

FIG. 1. Luminescence spectrum, at 1.5 °K, of ion-bombarded crystal annealed at 1300 °C. The zero for the phonon-energy scale is the no-phonon line at 6279.8 Å. Maxima in the lattice density of states at X and L are indicated above the spectrum.

TABLE I. Cubic SiC phonon energies (in meV) at X, L, and Γ. The data are taken from Refs. 11 and 12.

	X	L	Γ
TA	46.3	32.5	
LA	79.4	75.6	
TO	94.4	95.0	98.7
LO	102.8	103.9	120.5

The expected positions in the spectrum of Γ, X, and L phonons are indicated in Fig. 1. A phonon-energy scale shows energy in meV as measured from the no-phonon line at 6279.8 Å. The gap between acoustic and optic branches is thought to extend from about 80 to 91 meV. This gap is due to the considerable Si to C mass ratio.

The sample of Fig. 1 was bombarded with 120-keV He^+ ions (10^{14} cm^{-2}) and annealed at 1300 °C. The luminescence spectrum was measured at 1.5 °K. The two-phonon spectrum (not shown) is moderately strong.

It is observed that there are prominent peaks close to the positions expected for the zone center (Γ) TO and LO phonons. Most of the other peaks show little relationship to the probable density of states for the cubic SiC lattice. The 83-meV mode falls in the gap and can therefore be considered a localized mode.[13] The rest of the structure is in-band, with peaks strongly displaced from the X and L density-of-states maxima. This is especially apparent at the positions of LA(X), LO(X), and LO(L). The strong resonant mode at 66.5 meV falls within the LA branch. Its energy is that expected for an LA mode with a wave vector about $\frac{2}{3}$ of a Brillouin-zone boundary wave vector. Measurements at higher temperature (Sec. V) suggest that this mode plays a role in the Jahn-Teller effect.

IV. TEMPERATURE DEPENDENCE

The luminescence spectrum of Fig. 1 has an unusual temperature dependence, involving two abrupt changes in the interval 1.3–13 °K. Thus, we observe three spectra, called L, M, and H for the low- (1.3 °K), medium- (2 °K), and high- (> 13 °K) temperature ranges in which they predominate. The vibronic components are nearly the same in all three spectra, with the exception of the 66.5-meV resonant mode.

For describing the changes with temperature, it is sufficient to discuss only the no-phonon lines, shown schematically in Fig. 2. It is not unusual to observe thermal activation of higher-energy initial states, but Fig. 2 indicates that the *L* spectrum is extinguished as *M* is activated, and that *M* is extinguished as *H* is activated. At 77 °K (not shown) we observe a strong *H* spectrum with only a faint indication of *M*. At this temperature the *H* no-phonon line is broad, and is shifted to about 6273 Å. A model that can explain two successive switches in the phonon energy is one in which the luminescence center undergoes two configurational changes with changing temperature. Jahn-Teller distortions appear to offer the best explanation for the observed changes.

Tentatively, we may ascribe the three spectra to the three configurations listed in Table II. If this explanation is correct, the Jahn-Teller reduction of the initial-state energy is only 3.2 meV, and the barrier between equivalent Jahn-Teller minima is 0.7 meV. For the emission of the *L* spectrum our model requires a single Jahn-Teller configuration to be frozen in for times longer than the lifetime of the photon-emitting state. The *M* spectrum is observed at a higher temperature when several equivalent Jahn-Teller minima are shared during the lifetime of the photon-emitting state. This requires thermal activation over the 0.7-meV barriers between the minima. The *H* spectrum is observed when higher-energy configurations are activated, so that the distortion averages out over the initial-state lifetime. It should be remembered that the thermally determined state is the initial, or photon-emitting, state, not the ground state that would be studied in electron paramagnetic resonance.

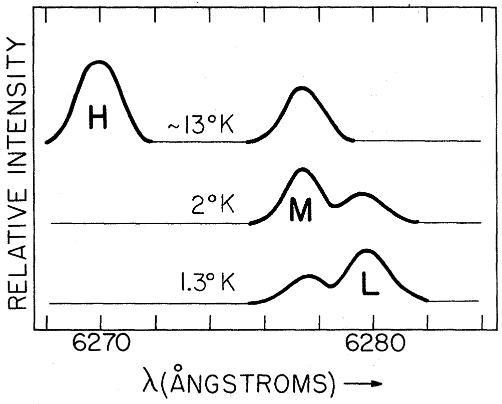

FIG. 2. No-phonon lines at three temperatures (schematic). The predominant line is *L* (low) at 1.3 °K, *M* (medium) at 2 °K, and *H* (high) at 13 °K. *L* is absent at 13 °K, and *M* disappears at a higher temperature. The changes are attributed to the Jahn-Teller effect.

TABLE II. Proposed configurations for the luminescence center at the three temperatures of Fig. 2.

T (°K)	Spectrum	No-phonon line (Å)	Activation energy (meV)	Proposed configuration
1.3	*L*	6279.8		Static Jahn-Teller
2	*M*	6277.6	0.7	Dynamic Jahn-Teller
13	*H*	6269.5	3.2	Undistorted

We have observed some sample to sample differences in the proportions of *L* and *M* spectra at a given temperature. In particular, the He^+-implanted samples have a larger proportion of *L* than the electron-irradiated samples, and the *L* line is somewhat broader. We attribute this difference to random strains in the thin He^+-implanted layer, for such strains favor one of the several equivalent Jahn-Teller distortions.[7] Thus, a strained crystal requires a higher temperature to pass to the dynamic Jahn-Teller range in which all the equivalent positions are shared. For this reason Fig. 1 shows mostly the *L* spectrum. An electron-irradiated sample shows approximately equal *L* and *M* doublets at 1.6 °K.

The activation energies of 0.7 and 3.2 meV for the *M* and *H* spectra, respectively, are obtained from the energy separations of the no-phonon (or other) lines, on the assumption that the luminescence transitions in all three configurations are to the same final state.

The ratio of *M* and *L* intensities, as a function of temperature, was measured for the crystals that appeared to be most free of strain. With $E = 0.7$ meV, we found the intensity ratio to be given approximately by

$$I_M/I_L = 100e^{-E/kT} .$$

The preexponential factor of 100 is *not* attributed to a ratio of oscillator strengths for the reasons given in Sec. VI. Instead, it may represent the ratio of a lattice frequency to the electron-hole recombination frequency. Another possibility is that the number 100 is a density-of-states factor, being the ratio of vibrational modes compatible with the *M* configuration to those compatible with the frozen-in *L* configuration.

The thermally broadened *H* spectrum at 77 °K and higher is the one previously reported by Geitsi *et al.* (called "*A*"), and perhaps by Makarov,[14] although the latter gave 1.964 eV as the energy of the no-phonon line. Geitsi *et al.* also report that a faint *A* spectrum is sometimes seen in unirradiated samples.[15]

V. 66.5-meV RESONANT MODE

Figure 3 shows the luminescence at 45 °K. The

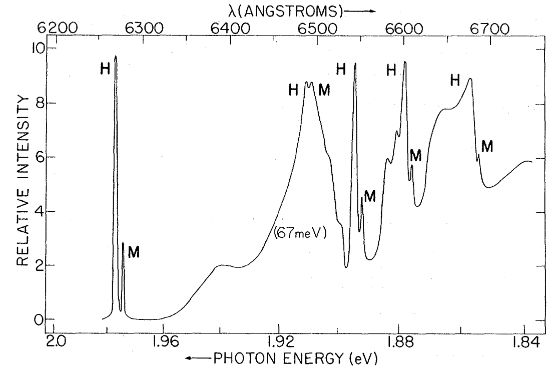

FIG. 3. Luminescence spectrum at 45 °K. At this temperature the *H* spectrum is much stronger than the *M* spectrum, except for the 66.5-meV mode which is thought to couple to the Jahn-Teller distortion.

spectrum *L* has been quenched, and *H* is now much stronger than *M* except for the 66.5-meV resonant mode. This seems to indicate a strong coupling of the 66.5-meV mode not only to the *M* configuration but also to *L*, for the *L* and *M* vibronic components are all of comparable strength. If the proposed configurations of Table II are correct, we are led to the conclusion that the electron-vibrational coupling that produces the Jahn-Teller distortion involves the 66.5-meV mode. However, the strength of the *M* resonant mode is not really known, for it stands on top of the LA continuum of the *H* spectrum. We must therefore also consider whether the resonant mode can produce the required distortion. In the following paragraphs the magnitude of the phonon energy will be made plausible on the assumption that the luminescence center is an impurity-vacancy complex on nearest-neighbor sites. This is the Watkins-Corbett model[5] that was shown to be appropriate for several persistent defects in Si.[3]

The Jahn-Teller distortion found for the phosphorus-vacancy complex[5] in Si is one in which a pair of Si atoms form a bond and pull together in a ⟨110⟩ direction, thereby reducing the symmetry of the complex from C_{3v} to C_{1h}. In SiC the atoms pulling together would be either a C or a Si pair, but the direction is ⟨110⟩ in either case, and a lattice phonon making a large contribution to such a distortion would be a LA mode whose adjacent antinodes lie at the positions of the Si or C pair. We shall estimate the energy of this lattice mode.

The mode in question has a half-wavelength $\lambda/2$, equal to $a/\sqrt{2}$, the pair separation, where a is the lattice constant. The corresponding wave number $k(\mathrm{JT})$ is

$$k(\mathrm{JT}) = 2\pi/\lambda = \sqrt{2}\,\pi/a \ .$$

The phonon energies have not been measured in the [110] direction, but the LA anisotropy is thought to be small enough to make a comparison with [111] phonons meaningful. The energy of a [111] phonon with a wave vector having the same magnitude as $k(\mathrm{JT})$ is about 71 meV.[12] An alternate estimate of the energy considers the fact that the $k(\mathrm{JT}) \approx 0.67k(K)$ and takes the energy of the phonon whose wave number is $0.67k(L)$, where K and L are the Brillouin-zone boundary positions in the [110] and [111] directions, respectively. This energy is about 63 meV.[12] Thus, the resonant mode of 66.5 meV falls between the two estimates, and we can say that it has approximately the expected energy if it is to produce the kind of distortion observed in Si impurity-vacancy complexes.

Summarizing, a model for the radiation defect reported here should be compatible with a Jahn-Teller effect and with the stability of the defect against a 1600 °C anneal. The extensive work on irradiated Si suggests that the luminescence center may be an impurity-vacancy complex, and a strong resonant mode observed in the vibronic spectrum appears to be consistent with the form of distortion found in such complexes. However, more work should be done to confirm the model, and to identify the impurity.

VI. A REJECTED MODEL

Finally, we consider an alternative explanation of the temperature dependence that does not invoke the Jahn-Teller effect. It is possible to arbitrarily assign oscillator strengths to the *L*, *M*, and *H* transitions in the ratios 1 : 100 : 1500. These ratios would satisfy our observations on the *no-phonon* lines, assuming the intensity to be determined by an exciton capture rate independent of temperature. Thus, the *L* transition may be forbidden, but it would nevertheless appear at very low temperatures because of the improbability of decay through the faster but more energetic *M* and *H* states. At a higher temperature, *M* and *H* transitions would be relatively strong enough that *L* would seem to be quenched. At a still higher temperature only the *H* spectrum would have appreciable strength.

However, the above scheme fails to explain the constant ratio of vibronic to no-phonon intensities in all three spectra *L*, *M*, and *H*; for the vibronic components of *L* would not in general be as strongly forbidden as the *L* no-phonon line. This follows from the fact that the phonon coupling is moderately strong, and the forbidden *L* transition could therefore be circumvented by emission of a phonon having the proper symmetry to make the vibronic transition allowed.

The most common examples of the above in the zinc-blende semiconductors are the *j*-*j*-coupled exciton states in which the $J = 2$ forbidden state (B) has a lower energy than the $J = 1$ allowed state

(A).[16,17] In both GaP : Bi and GaP : N this leads to a ratio of vibronic to no-phonon components that is much greater for the B spectrum. The absence of comparable ratio changes in our L, M, and H spectra indicates that the oscillator strength scheme is not satisfactory, and it leaves us with the Jahn-Teller effect as the most probable explanation of the unusual temperature dependence.

Note added in proof. A true Jahn-Teller effect requires the degeneracy of the electronic wave function. In the present case we have no independent evidence of such degeneracy. In the absence of degeneracy a low-temperature lattice distortion may occur nevertheless, and it is sometimes called a pseudo-Jahn-Teller effect.

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Photoluminescence Processes in $In_{1-x}Ga_xP$ at 2°K

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Photoluminescence measurements on $In_{1-x}Ga_xP$ have verified the location of the direct-indirect conduction-band crossover at $x = 0.74$, $E_g = 2.33$ eV at 2 °K. The photoluminescence spectra observed are InP-like for $x < 0.68$ and GaP-like for $x > 0.72$. Shallow bound excitons are observed with indirect gap $In_{1-x}Ga_xP$. Curvature in the relationship between the bound exciton energy and alloy composition suggests curvature of the indirect Γ_{8v}-X_{1c} band gap as a function of alloy composition (maximum deviation from the linear dependence is estimated at 22 meV). Shallow donor states seem to be tied rigidly to their conduction bands. No mixing of the Γ and X conduction-band donor ground states has been observed. Thus, significant mixing occurs over a range less than $\Delta x = 0.02$, the compositional resolution in the present measurements.

I. INTRODUCTION

We present here the results of a study of the photoluminescence (PL) of $In_{1-x}Ga_xP$ at 2 °K. The results give an understanding of the luminescence processes that occur in $In_{1-x}Ga_xP$ and other III-V alloys in general, especially with respect to the changes in luminescence mechanisms that occur concurrently with the crossover between the direct and indirect conduction bands. At the same time this study has furnished precise data on the behavior of impurity states in the alloy. Low-tem-