Pressure dependence of deep electronic levels in semiconductors: Phosphorus-vacancy pair (or Si *E* center) and divacancy in silicon

G. A. Samara
Sandia National Laboratories, Albuquerque, New Mexico 87185
(Received 17 January 1989)

The effects of hydrostatic pressure on the electron thermal emission rates and capture cross sections of three deep electronic levels in phosphorus-doped silicon were investigated. Included were the $E_c - 0.44$ eV acceptor associated with the phosphorus-vacancy pair defect (or Si E center), the $E_c - 0.23$ eV acceptor associated with the $2-/-$ charge state of the divacancy, and a level of uncertain origin at $E_c - 0.40$ eV. The results allow determination of the shift of the energies of these levels with pressure and of the breathing-mode lattice relaxations which accompany electron emission and capture by these levels. This is the first determination of these properties. For the phosphorus-vacancy acceptor, pressure shifts the level deeper into the band gap, and an outward (inward) volume relaxation accompanies electron emission (capture). These results can be qualitatively understood in terms of the accepted model for this defect and the bondinglike nature of its level. Qualitatively similar results are obtained for the $E_c - 0.40$ eV level, but opposite effects are seen for the divacancy level. Specifically, with pressure, this latter level moves higher in the band gap, and the lattice relaxes inward (outward) on electron emission (capture). These results can also be understood in terms of the accepted model for the defect and the antibondinglike nature of its level.

I. INTRODUCTION

The vacancy and vacancy-related defects in silicon (Si) are among the most important and fundamental defects in covalent semiconductors. Knowledge of their properties is basic to the understanding of many electronic phenomena, defect interactions, diffusion, annealing, and substitutional impurities in Si.[1] These defects are generally introduced during growth and advanced microelectronic fabrication which involves such steps as ion implantation, plasma etching, and energetic beam lithographies; however, their controlled introduction and study most often rely on the use of irradiation by electrons, photons, or neutrons.

One very important manifestation of these defects is the deep electronic levels they introduce into the band gap. These levels act as carrier traps and recombination centers and strongly influence the electronic properties. Although research on these defects and associated energy levels has been an active area for over 30 years, our knowledge of the subject is incomplete, and some of the more recent research[2–6] points to the complexity of some of the phenomena involved.

We have been investigating the effects of hydrostatic pressure on impurity and defect levels in Si and other semiconductors.[7–9] The work is motivated by the expectation that pressure results can lead to a better understanding of the physics of such levels. In particular, pressure modifies deep-level potentials and makes it possible to test proposed models and/or aid in the identification of the microscopic defects responsible for the deep levels. Additionally, pressure results contain information on the breathing-mode lattice relaxation associated with both the formation of defects and with the emission and capture of carriers at deep levels.

In the present paper we report and discuss the effects of pressure on the properties of three deep levels in phosphorus (P) -doped Si. Two of these levels are associated with vacancy-related defects: the phosphoros-vacancy (P-V) pair defect, or Si E center, and the Si divacancy (V-V). The third level, whose signature in deep-level transient spectroscopy (DLTS) data is partially hidden on the low-temperature side of the P-V pair peak, may be one of the configurations of the newly recognized[3–5] multistable defect in P-doped Si.

The P-V pair defect has long been recognized as the dominant observable defect produced by high-energy electron or photon irradiation of *P*-doped float-zone Si. It produces an acceptor deep level located 0.44 eV below the conduction-band edge, E_c, i.e., at $E_c - 0.44$. (Unless otherwise specified, all energies in this paper are in units of eV.) Early EPR studies by Watkins and Corbett[10] showed that this defect is formed by the trapping of a mobile lattice vacancy next to a substitutional P impurity atom. The defect also has what had been thought to be a well-recognized spectrum in DLTS. However, recent DLTS studies have revealed unexpected behavior under minority carrier injection[2] and shown[3,4] that this spectrum hides under it another peak which is now believed to be associated with a substitutional phosphorus–interstitial-carbon (P-C_i) pair defect[5] and which displays a number of metastable configurations. There is still some uncertainty and disagreement about the properties of this defect,[3–5] but its discovery has emphasized the important role of carbon, when present, in the defect structure and kinetics of irradiated *n*-type sil-

 ©1989 The American Physical Society

icon. The third level in our present data at $\sim(E_c-0.40)$ may be associated with one of the configurations of this defect.

The divacancy is an intrinsic defect in Si produced by high-energy particle irradiation and consists of two vacant nearest-neighbor lattice sites each surrounded by three occupied lattice sites.[11] It introduces three deep levels in the band gap, with four possible charge states acting either as a single donor or as a double acceptor. Although the defect has been studied extensively by a wide variety of techniques,[12] uncertainties remain about the identification and positions of its energy levels, particularly the acceptor levels. On the basis of defect introduction rates and annealing studies, the two electron traps seen in deep-level transient spectroscopy studies at $E_c-0.23$ and $\sim(E_c-0.41)$ have been attributed to different charge states of the same defect, and it has been further suggested[13] that this defect is the divacancy, the two levels corresponding to the $2-/-$ and $-/0$ charge states, respectively. The $E_c-0.23$ level was well resolved in the present study, but the $E_c-0.41$ level was hidden under the P-V pair peak.

In what follows we summarize the experimental details in Sec. II, and this is followed by presentation and discussion of the results in Sec. III. Section IV provides some concluding remarks.

II. EXPERIMENTAL DETAILS AND DATA ANALYSIS

The deep levels examined in the present work were studied by transient capacitance[14] and DLTS (Ref. 15) techniques, the measurements being done in the depletion region of reverse-biased p^+/n junction diodes. The diodes were cut from Si solar cells in which the n region was P-doped (5×10^{15} cm^{-3}), flat-zone Si, and the p region was doped with boron at $\sim5\times10^{18}$ cm^{-3}. The defects were introduced by γ irradiation (^{60}Co source) of the diodes at room temperature to a total dose of $(1-2)\times10^8$ rads. After irradiation the diodes were stored at room temperature for many weeks before the measurements were made.

Capacitance transients and DLTS spectra were measured as functions of temperature and pressure. The measurements were performed at reverse biases of 2 and 4 V and yielded the electron thermal emission rates (e_n), emission energies, and their pressure dependences. The effects of electric field in the depletion region on these properties were negligible for our present purposes over this range of bias voltages. The pressure dependence of the electron capture cross section was determined from the variation of the initial capacitance amplitude after reverse bias and from the variation of the amplitude of the DLTS peak as functions of the length of the trap-filling pulse.[7,15]

All temperature and pressure measurements were made with the sample mounted inside a 10-kbar pressure cell which was in turn mounted in a conventional low-temperature Dewar. The temperature could be either varied between 77 and ~350 K at different rates or accurately controlled at a fixed T (to better than 0.1 K) over the available pressure range. Helium was the pressurizing medium, and the pressure was measured to better than 1% by a calibrated manganin gauge. Temperature was measured using Cu-Constantan thermocouples.

The primary data generated in the present work are the electron thermal emission rates (e_n) and capture cross sections (σ_n) and their pressure and temperature dependences. The data are analyzed and interpreted in terms of the detailed balance result

$$e_n=\sigma_n\langle v_n\rangle N_c\exp(-\Delta G/kT)$$
$$=\sigma_n\langle v_n\rangle N_c\exp(\Delta S/k)\exp(-\Delta H/kT) \qquad (1)$$

following procedures discussed earlier.[7,8] In Eq. (1) $\langle v_n\rangle$ is the average electron thermal velocity, and N_c is the effective density of states in the conduction band. The product $\langle v_n\rangle N_c$ is proportional to $m_n^*T^2$, where m_n^* is the electron effective mass. The pressure dependence of m_n^* is negligibly small.[7,8] ΔG is the change in Gibbs free energy which accompanies the emission of the electron from the deep level. It can be expressed in terms of the enthalpy (ΔH) and total entropy (ΔS) changes accompanying electron emission, since $\Delta G=\Delta H-T\Delta S$. As will be shown later, for the deep levels of interest in this work, σ_n is found to be independent of pressure (P), and thus to a good approximation Eq. (1) yields[8]

$$(\partial \ln e_n/\partial P)_t=-(kT)^{-1}(\partial\Delta G/\partial P)_T\ . \qquad (2)$$

It is thus seen that measurements of e_n versus P at constant T yield $\Delta G(P)$ whereas measurements of e_n versus T at constant P plotted as $\ln(e_nT^{-2})$ versus T^{-1} at different pressures yield $\Delta H(P)$. Knowing both $\Delta G(P)$ and $\Delta H(P)$ fixes $\Delta S(P)$. Finally, it can be easily shown that[8]

$$(\partial\Delta G_n/\partial P)_T=\Delta V_n \qquad (3)$$

where, in the absence of a barrier to electron capture (as is the case for the present levels), the thermodynamic volume change ΔV_n can be interpreted as the volume change, or breathing-mode relaxation, of the defect which accompanies electron emission. In using Eq. (3), the experimentally determined $(\partial\Delta G/\partial P)_T$ needs to be corrected for the pressure dependence of ΔG of the band gap,[16] and, to emphasize this point, we designate the corrected quantity in Eq. (3) by the subscript n.

III. RESULTS AND DISCUSSION

A. DLTS spectral features

The solid lines in Fig. 1 show a typical atmospheric pressure (1 bar) DLTS spectrum due to majority carrier traps for the samples used in the present study. The spectrum is in many respects similar to what has been reported earlier[2–4] and reveals several deep levels whose energies below the conduction-band edge (E_c) are indicated. The $E_c-0.17$ level is associated with the oxygen-vacancy pair (or Si A center) acceptor. It will not be discussed further in the present paper because the pressure dependence of its properties was reported earlier.[8] The

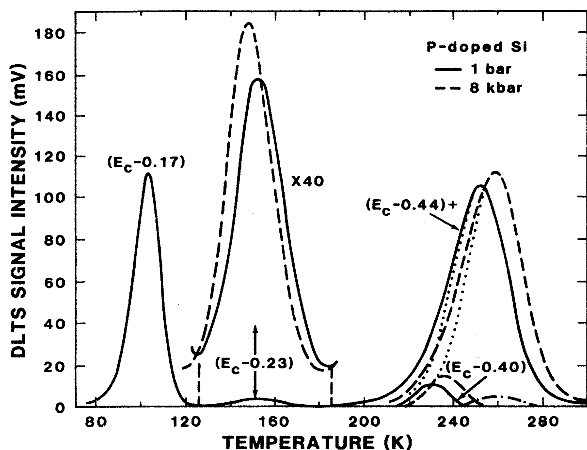

FIG. 1. DLTS spectrum of a phosphorus-doped, float-zone-grown silicon after γ irradiation (rate window is 2560 s^{-1}). The effect of pressure on some of the peaks is indicated.

$E_c - 0.23$ peak is believed to correspond to the $2-/-$ charge state of the divacancy acceptor level. As we shall see, annealing studies and the pressure results are consistent with this assignment. Finally, the spectrum labeled $(E_c - 0.44)+$ (represented by the solid line, and where the + symbol indicates that the spectrum is associated with more than one defect) is the signature which has long been associated with the P-V (or Si E center) acceptor. However, there is a very noticeable asymmetry on the low-temperature side of this spectrum as indicated by the dotted line in Fig. 1. Subtracting this asymmetry reveals the small peak centered at 230 K (solid line) whose corresponding level (uncorrected for possible capture barrier) is at $\sim(E_c - 0.40)$. We shall return to this feature shortly.

The $(E_c - 0.44)+$ spectrum also hides under it the small peak centered at 260 K (dot-dashed curve) and associated with a level at $\sim(E_c - 0.41)$. We deduced this peak from annealing studies. After annealing the samples under reverse bias (-6 V) at 383 K for 30 min, the only features of the spectrum that remained are the $E_c - 0.17$ Si A center peak, the $E_c - 0.23$ peak, and this $E_c - 0.41$ peak. The intensity of this latter peak is as shown in Fig. 1 and is a little higher than that of the $E_c - 0.23$ peak. The occurrence of the $E_c - 0.23$ and $E_c - 0.41$ peaks together after annealing allows their identification, following earlier results,[13] as the two acceptor levels of the Si divacancy, the first being associated with the $2-/-$ charge state and the second with the $-/0$ charge state.

Returning to the $E_c - 0.40$ peak in Fig. 1, we believe that this feature may be related to one of the configurations of the newly recognized[3-5] multistable defect in P-doped Si which is now believed[5] to be the P-C_i pair defect. This latter defect was revealed in DLTS scans after the sample had been annealed at constant temperature for 5 to 10 min under minority carrier (hole) injection.[3-5] Earlier isothermal minority carrier injection studies by Barnes and Samara[2] produced decreases in the intensity of the Si E center spectrum which were thought to result from recombination-enhanced annealing of this center. However, more detailed later studies revealed the presence of this new defect. In the work of Song *et al.*[3] one signature of the defect after hole injection annealing was a decrease in the intensity of the $(E_c - 0.44)+$ peak and an asymmetry and weak shoulder on the low-temperature side of this peak. Subtracting the spectrum after annealing from that before annealing revealed two peaks with $E_c - 0.44$ and $E_c - 0.34$ (uncorrected for possible capture barriers) which were taken to be two configurations of the new defect. Chantre *et al.*[4] demonstrated the existence of the new defect by similar spectral subtraction. Their DLTS spectrum after hole injection annealing was somewhat different from that of Song *et al.*[3] and after subtraction it revealed a new peak with $E_c - 0.30$ which is now believed to be one of the configurations of the P-C_i defect.[5]

The relative intensity and location in temperature of the $E_c - 0.40$ peak in Fig. 1 (obtained without minority carrier injection) resemble those of the $E_c - 0.34$ peak in the work of Song *et al*;[3] however, obviously the energies of the two peaks differ considerably. We assign a rela-

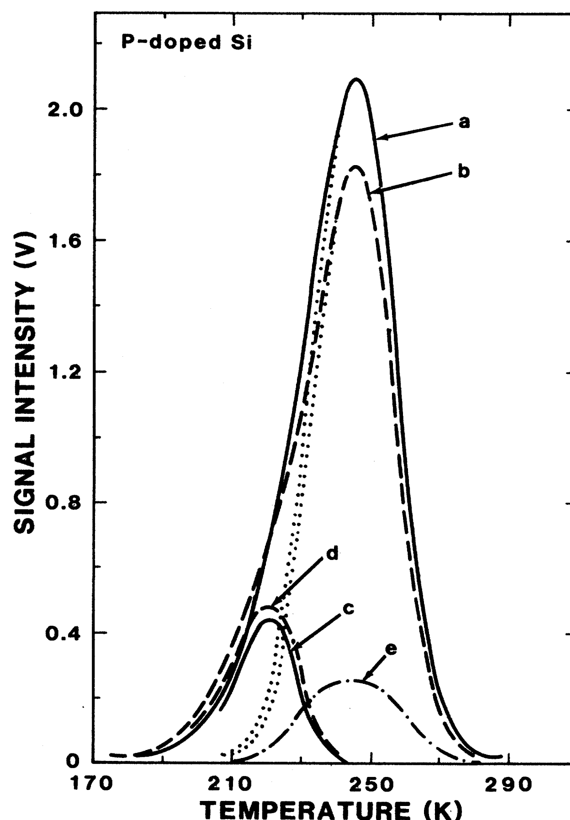

FIG. 2. The effect of minority carrier (hole) injection (0.5 A/cm^2 for 10 min at 250 K) on the DLTS spectrum in the vicinity of phosphorus-vacancy peak (see text for details). (Rate window is 1280 s^{-1}.) No further changes were observed by injection at higher current densities and for longer times. The spectra are resolved into their various components.

tively large uncertainty (±0.03 eV) to the $E_c-0.40$ level in our data to reflect the maximum possible uncertainty associated with the spectral subtraction used to reveal it. To pursue the nature of this level further, we have examined the effects of forward bias annealing on the intensity and shape of the DLTS spectrum. Some of the results are shown in Fig. 2. Curve *a* is the spectrum before annealing and curve *b* is the spectrum after annealing for 10 min at 250 K and 0.5 A/cm^2 constant forward current. Repeating this anneal for an additional 20 min under the same conditions and then for 20 more minutes at 250 K and 1.5 A/cm^2 did not yield any change in curve *b*. Comparing curves *a* and *b* shows a decrease in the amplitude and an increase in the low-temperature asymmetry of the spectrum, changes qualitatively similar to, but less in magnitude than, those reported by Song *et al.*[3] and Chantre *et al.*[4,5] The differences in magnitude between the results undoubtedly reflect differences in the concentration of the new defect.

Curves *c* and *d* in Fig. 2 are obtained from curves *a* and *b*, respectively, by subtracting the asymmetry at the low-temperature side of the spectra. Although peak *d* appears at a slightly lower temperature (1–2 K) than peak *c*, the characteristics of the two peaks are similar (and comparable to the $E_c-0.34$ peak reported by Song *et al.*[3]), and both appear to correspond to the same defect with a level at $E_c-0.40\pm0.03$. The defect may be one of the configurations of the P-C$_i$ pair defect. However, one puzzle is the relatively large difference in the energy of our level compared to that of Song *et al.* Clearly more work is needed to resolve the difference.

The results in Fig. 2 also show that subtracting the symmetric part of curve *b* from that of curve *a* reveals peak *e* which occurs at the same temperature and corresponds to the same level energy, $E_c-0.44$, as the P-V pair. This feature has been observed by Song *et al.*[3] and is thought to correspond to another of the configurations of the P-C$_i$ defect. Finally, it is noted, as is evident from the above discussion, that, for our samples, the bulk of the intensity under the $(E_c-0.44)+$ spectrum in Fig. 1 is associated with the $E_c-0.44$ P-V pair level.

In what follows in this paper we present and discuss the effects of pressure on the following three levels: the P-V pair level at $E_c-0.44$, the new level at $E_c-0.40$, and the divacancy level at $E_c-0.23$. Similar studies of the various multistable configurations of the new P-C$_i$ pair defect will be the subject of a future investigation.

B. Electron thermal emission rates and energies

1. $E_c-0.44$ P-V acceptor

The electron thermal emission rate from the P-V pair acceptor decreases with pressure. This decrease can be deducted from the pressure shift of the DLTS spectrum (e.g., Fig. 1) and from capacitance transients measured as a function of time after the application of reverse bias. Figure 3 shows normalized transient data at 260 K and different pressures displayed on a semilogarithmic plot.

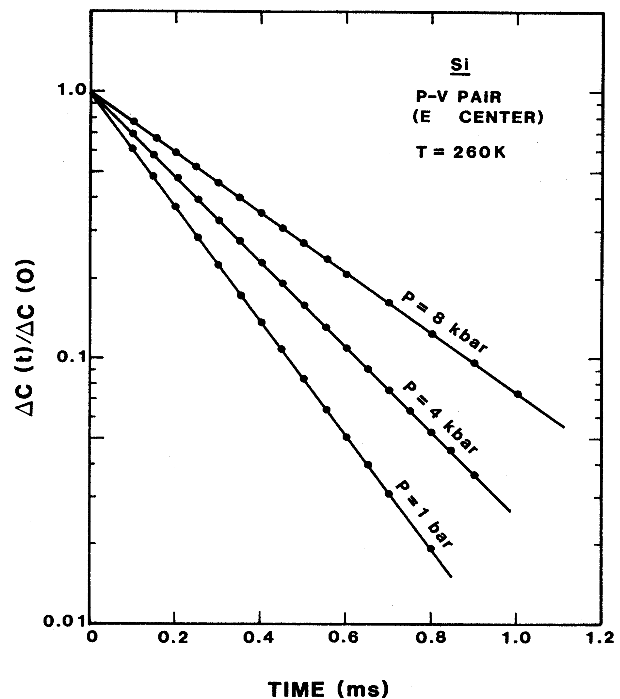

FIG. 3. Normalized capacitance transients for electron emission from the phosphorus-vacancy acceptor level in silicon measured at different pressures. The slope of each line yields the thermal emission rate which is seen to be strongly pressure dependent.

The exponential decay of the capacitance is clearly evident. The slope of each straight line in the figure yields e_n at 260 K and the indicated pressure. Figure 4 shows that e_n decreases logarithmically with pressure as observed earlier for other deep levels.[7,8] The slope $[(\partial \ln e_n/\partial P)_T]$ decreased monotonically in magnitude from $-(8.2\pm0.5)\%$ kbar^{-1} at 220 K to $-(6.8\pm0.5)\%$ kbar^{-1} at 280 K.

The decrease of e_n with pressure is also reflected in constant-pressure Arrhenius plots of $\log_{10}(e_n/T^2)$ versus T^{-1}. Two such plots are shown in Fig. 5. The slopes of these plots yield the activation enthalpy, ΔH ($=E_c-E_T$, where E_T is the deep level, or trap, energy below E_c) of the emission process. ΔH increases with pressure from 445 meV at 1 bar to 458 meV at 8 kbar. Figure 6 contrasts the pressure shift of the P-V acceptor level with that of the silicon band gap E_g, and also with the shift of the $E_c-0.23$ deep level to be discussed below. The slope for the P-V level is 1.4±0.4 meV kbar^{-1}, which implies that this level moves away from E_c at a rate of 1.4 meV kbar^{-1}. The shift of the gap is[16,17] $dE_g/dP=-1.5$ meV kbar^{-1}. Combining these two results shows that E_T moves closer to E_v (the valence-band edge), and therefore deeper into the gap, at a rate of 2.9 meV kbar^{-1}.

The P-V acceptor is thus not pinned to either E_c or E_v. This is what we expect for a deep level.[7] The fact that the level moves deeper in the gap reflects its more stable

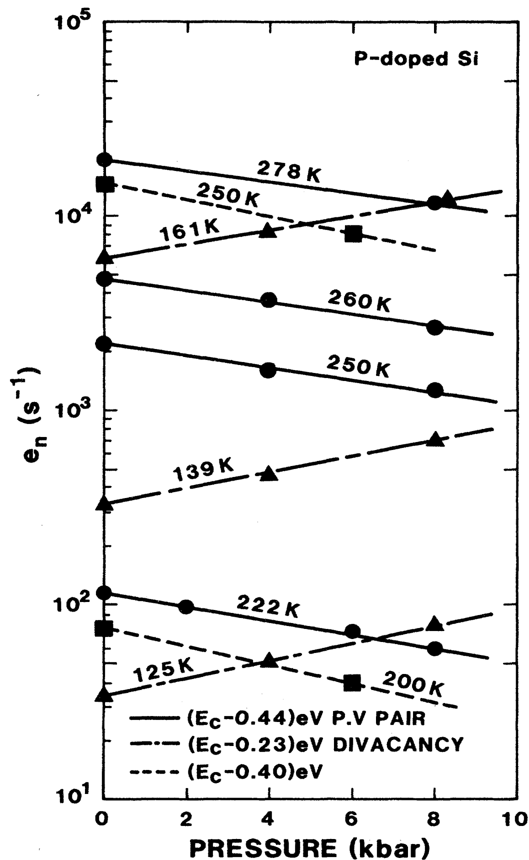

FIG. 4. Pressure dependence of the electron thermal emission rates from various centers in γ-irradiated, phosphorus-doped, float-zone Si.

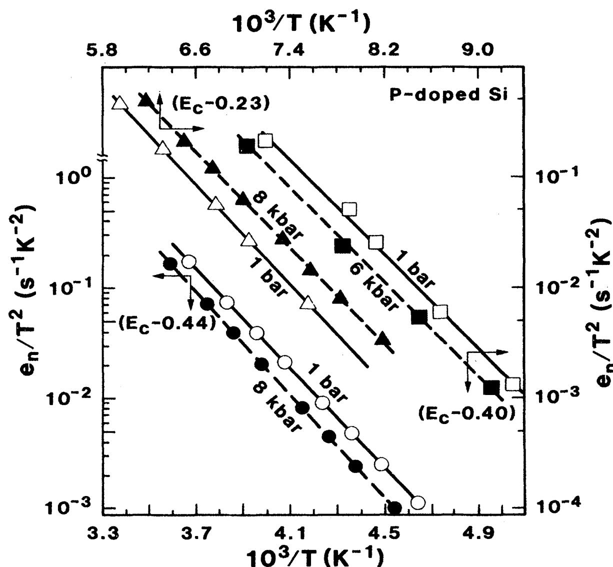

FIG. 5. Temperature dependence of the electron thermal emission rates from various centers in γ-irradiated, phosphorus-doped, float-zone Si.

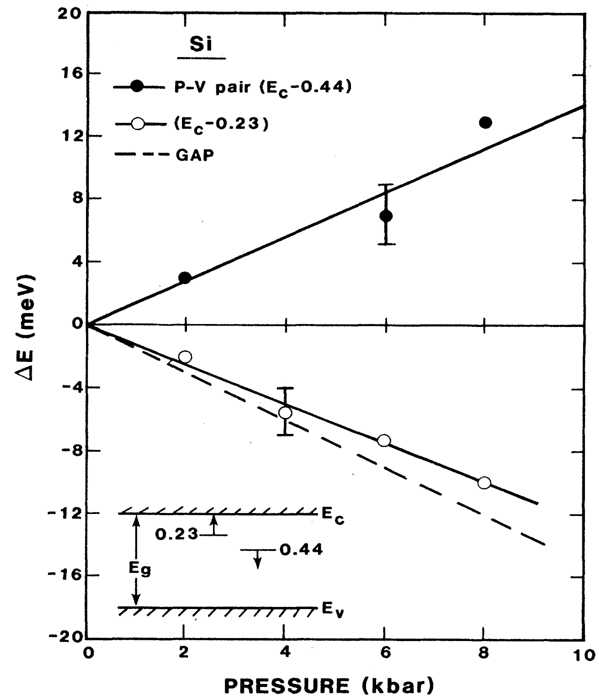

FIG. 6. Pressure dependences of the activation energies $E_c - E_T$ (or ΔH), for the phosphorus-vacancy $E_c - 0.44$, and divacancy, $E_c - 0.23$, acceptors in Si. The shift of the Si band gap is shown for comparison. The inset indicates that with pressure the 0.44-eV level moves deeper in the gap, whereas the 0.23-eV level moves higher.

bonding character at high pressure, as will be discussed later.

2. $E_c - 0.23$ V-V acceptor

Unlike the behavior of the P-V acceptor, e_n for the $E_c - 0.23$ divacancy level increases with increasing pressure at constant T as can be seen from the results in Figs. 4 and 5. The slope $(\partial \ln e_n / \partial P)_T$ decreases in magnitude from 10.4% kbar^{-1} at 125 K to 8.3% kbar^{-1} at 160 K. The activation enthalpy, ΔH $(= E_c - E_T)$, deduced from Arrhenius plots such as those in Fig. 5, decreases at a rate of -1.2 ± 0.3 meV kbar^{-1} as shown in Fig. 6. This shift, which is comparable to the shift of the gap, implies that E_T moves closer to E_c at a rate of 1.2 meV kbar^{-1}.

3. $E_c - 0.40$ acceptor

The pressure dependence of this level is qualitatively similar to that of the P-V acceptor but is opposite to that of the $E_c - 0.23$ V-V level. Some of the results on the $E_c - 0.40$ level are shown in Figs. 1, 4, and 5. Because of uncertainties associated with the spectral subtraction used to deduce the DLTS peaks for this level (see discussion above), there is more scatter in the $e_n(T)$ data for this level than for the other two levels in Fig. 5. The slope in Fig. 5 yields $\Delta H = 400 \pm 30$ meV at 1 bar. Because of this relatively large uncertainty in ΔH, it was not

possible to determine the pressure dependence of ΔH with certainty. However, we believe that ΔH increases with pressure as in the case of the P-V acceptor. It is certainly clear from Fig. 4 that e_n for the $E_c-0.40$ level decreases with pressure. Results at two temperatures are shown in Fig. 4 where the slope $(\partial \ln e_n/\partial P)_T = -(10.3\pm1.0)\%$ kbar^{-1} at 200 K and $-(9.8\pm1.0)\%$ kbar^{-1} at 250 K. Use of these slopes in Eq. (2) yields $(\partial\Delta G/\partial P)_T = 1.8\pm0.2$ meV kbar^{-1} at 200 K and 1.7 ± 0.2 meV kbar^{-1} at 250 K. These results almost certainly imply that ΔH also increases with pressure, and the $E_c-0.40$ level thus falls deeper in the gap.

C. Electron capture rates and cross sections

As is true for several other deep electronic traps in Si, the electron capture rates (τ_n) of the $E_c-0.44$ P-V and $E_c-0.23$ V-V levels do not exhibit any significant temperature or pressure dependences. These results lead to the conclusion[8] that the associated capture cross sections (σ_n) are also essentially independent of temperature and pressure. Some of the results follow.

Figure 7 shows a plot of $\log_{10}[1-\Delta C(0,\delta)/\Delta C(0,\rightarrow\infty)]$ versus δ at different pressures and temperatures for the P-V acceptor. In this representation $\Delta C(0)$ is the initial (i.e., $t=0$) amplitude of the capacitance transient after reverse bias, and δ is the trap-filling pulse width. Such a plot yields, over a range of δ, a straight line whose slope[7] is $-\tau_n$ which is related to σ_n by $\tau_n = n\langle v_n\rangle\sigma_n$. The results in Fig. 7 yield $\tau_n = 8\times10^6$ s^{-1}. From this value of τ_n and the known values of n $(=5\times10^{15})$ cm^{-3} and $\langle v_n\rangle$ $(=1.8\times10^7$ cm s^{-1} at 260 K) we obtain $\sigma_n \approx 1\times10^{-16}$ cm^2.

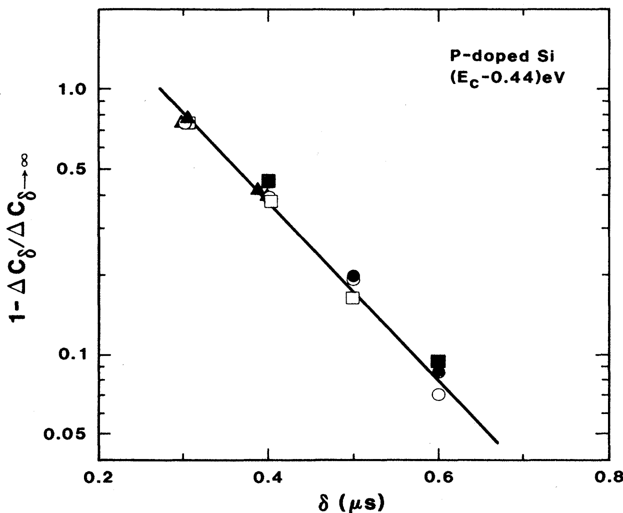

FIG. 7. Normalized initial capacitance amplitude after reverse bias as a function of filling pulse width δ for the $E_c-0.44$ P-V acceptor level in Si. The different symbols represent data at 0, 4, and 8 kbar and at 260 and 270 K at these pressures. Within the scatter of the data there are no discernible pressure or temperature effects.

Within the scatter of the data, the slope (or τ_n) in Fig. 7 is independent of temperature and pressure. Since $\langle v_n\rangle \propto T^{1/2}$—a weak T dependence, the temperature independence of τ_n implies that σ_n is also very weakly T dependent. Similarly, since the pressure dependence of the free-carrier density, n, at the temperatures of interest is very small, and $\langle v_n\rangle$ is expected to be very weakly pressure dependent,[7,8] the results in Fig. 7 indicate that σ_n is essentially independent of pressure, i.e., $(\partial \ln\sigma_n/\partial P)_T \approx 0$.

Figure 8 shows similar results for the $E_c-0.23$ V-V deep level. In this case the data were obtained from the variation of the DLTS peak amplitude (N) with δ. Data below $\delta=0.6$ μs have a slope $(=-\tau_n)$ equal to -1.0×10^{-6} s^{-1} which, with $\langle v_n\rangle = 1.44\times10^6$ cm s^{-1}, yields $\sigma_n = 1.4\times10^{-17}$ cm^2. For $\delta\geq5$ μs there is a long linear region with slope $\tau_n = 8.5\times10^4$ s^{-1}, and $\sigma_n = 1.2\times10^{-18}$ cm^2. For both regions the slopes are independent of pressure, which, on the basis of the arguments advanced above, implies that σ_n for this level is also independent of pressure.

Because the signature of the $E_c-0.40$ level is mixed with that of the P-V level, we did not attempt to measure σ_n for the former level. By analogy with many other deep levels in Si studied in this work and elsewhere,[7,8,16,18,19] we suspect that this σ_n may also be approximately independent of both temperature (T) and pressure (P). This lack of any appreciable T and P dependence for all of these levels is not fully understood, but it has been argued that these features can be understood in terms of electron capture by multiphonon emission (MPE).[7] The temperature independence of σ_n is a natural consequence of the MPE theory in the low-T regime, whereas the pressure independence is most likely due to cancelling small pressure effects among the various parameters determining σ_n.[7] The fact that σ_n is approximately independent of T and P makes interpretation of

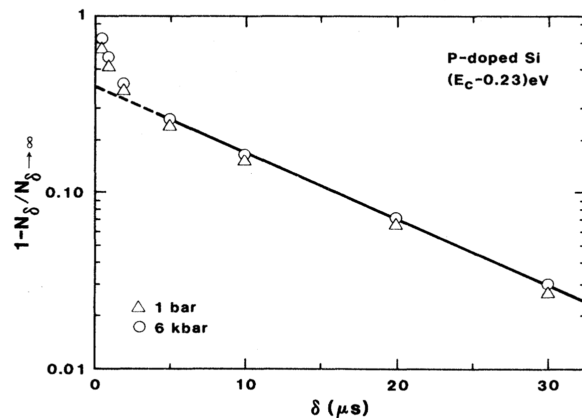

FIG. 8. Normalized DLTS peak amplitude as a function of filling pulse width δ for the $E_c-0.23$ divacancy acceptor in Si at 160 K and two pressures.

the $e_n(T,P)$ data in terms of changes in ΔG and ΔH more straightforward.

D. Lattice relaxation accompanying electron emission and capture

As mentioned in Sec. II and discussed elsewhere,[7,8,16] in the absence of significant pressure and temperature dependence of σ_n, the isothermal pressure dependence of e_n yields directly [via Eqs. (2) and (3)] the breathing-mode volume relaxation, ΔV_n, accompanying electron emission or capture. In this section we evaluate and discuss this relaxation for the three deep levels of interest.

1. The $E_v - 0.44$ P-V acceptor

Figure 9 shows ΔV_n versus T for the P-V acceptor. Within the accuracy of the data ΔV_n is independent of T over the limited T range covered. Two bounds for ΔV_n are shown in the figure: a lower bound represented by the data points and an upper bound represented by the dashed line. The reason for the two bounds has been discussed earlier,[16] and is briefly as follows. For the Si E center, electron emission is measured from the deep level E_T to the conduction-band edge, E_c, so that E_c is the reference energy state relative to which the change in ΔG_n between the two different charge states of the level is measured. However, since the energy gap of Si changes with pressure, $\partial \Delta G_{gap}/\partial P = -1.5$ meV/kbar,[8,17] the reference energy level, E_c, is not fixed, and its change contributes to the measured pressure dependence of e_n, and thereby ΔG_n. It is necessary to account for this contribution in order to determine the intrinsic pressure effect $(\partial \Delta G_n/\partial P)_T$ associated with the emission process. Unfortunately, it is not definitively established how much of the known shift of the Si gap is taken up by the motion of E_c and how much by the motion of E_v, thus, the two bounds in Fig. 9. The lower (upper) bound corresponds to the case where all of the shift of the gap is taken up by a shift in E_v (E_c) with E_c (E_v) remaining fixed.[16]

The results in Fig. 9 show that ΔV_n is positive implying that the lattice relaxes *outward* (i.e., expands) upon electron emission from the P-V acceptor level. We expect that an *inward* relaxation of the same magnitude would occur on electron capture. The sign of the relaxation can be qualitatively understood in terms of the physical model for the P-V center, as will be discussed below.

The magnitude of ΔV_n can be put in the proper perspective. The average of the two bounds in Fig. 9 is $\Delta V_n = 3.8$ Å^3 per emitted electron. In Si, the near-neighbor Si—Si bond length $r = 2.35$ Å, which we take to be also about the average distance between the vacancy of the P-V pair defect and its four nearest neighbors (see Fig. 10). A sphere of radius $r = 2.35$ Å around the vacancy has a volume $V_0 = 54.3$ Å. If to a first approximation all of the relaxation is taken up by the nearest-neighbor shell of atoms, then $\Delta V_n/V_0$ is $+7.0\%$. This corresponds to $\Delta r/r_0 = 2.3\%$, or an increase in r of 0.055 Å. This means that on electron emission the near-neighbor Si atoms relax outward by ~ 0.05 Å, which is quite substantial.

Our assumption that all of the relaxation is taken up by the first shell of Si atoms cannot be strictly correct; however, as discussed elsewhere,[8,16] it is not a bad approximation. We estimate that this assumption may lead to

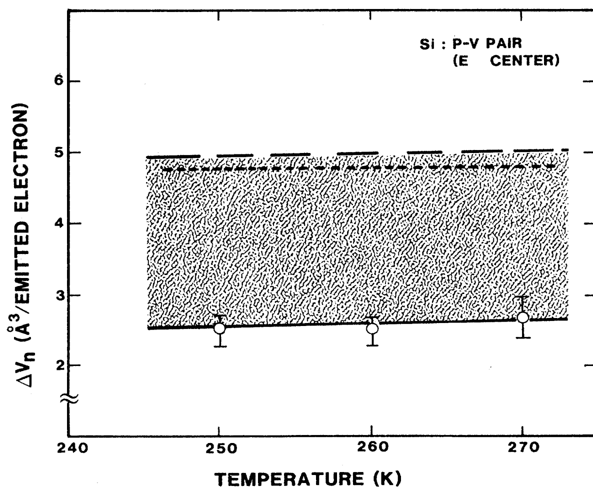

FIG. 9. Breathing-mode volume relaxation accompanying electron emission from the P-V acceptor in Si. The upper and lower bounds are discussed in the text. The dotted line represents the relaxation determined independently from annealing measurements (see text).

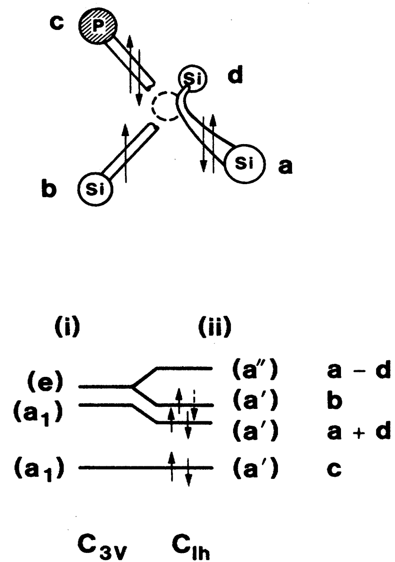

FIG. 10. Top: Model for the Jahn-Teller-distorted phosphorus-vacancy pair defect in Si. Bottom: Simplified molecular-orbital model of the electronic structure of the neutral defect, (P-V)^0, before (i) and after (ii) the Jahn-Teller distortion. In (ii) the linear combination of one-electron orbitals which form the various molecular orbitals are given. A captured electron (dashed arrow) goes into the bondinglike a orbital. (After Watkins and Corbett, Ref. 10.)

$\sim 30\%$ over estimate in the magnitude of Δr. Additionally, we have assumed that the breathing relaxation is symmetrical around the Si vacancy. This is, of course, not strictly correct since there is a Jahn-Teller distortion associated with the formation of the P-V center.[10] Despite these reservations, we believe that our above estimate correctly establishes the magnitude of Δr. Of course, the quantity directly evaluated from the experimental data is the volume relaxation, ΔV_n, and this evaluation represents the first determination of both the sign and magnitude of this relaxation for the P-V center.

Possible confirmation of the above sign and magnitude of ΔV_n for the P-V center may have come from a completely independent method. Barnes and Samara[20] have investigated the hydrostatic pressure dependence of the annealing kinetics of the P-V center in its neutral $(P\text{-}V)^0$ and negatively charged (P-V) states. The activation volumes associated with the defect annealing were found to be $\Delta V = -10.0$ Å^3/defect for $(\text{P-}V)^0$ and -5.2 Å^3/defect for $(\text{P-}V)^-$. These ΔV's represent the total volume changes associated with the annealing process which involve break-up of the defect and motion of the vacancy in addition to the annihilation of the defect. If it is assumed as a first approximation that these latter effects are comparable for the two charge states of the P-V center,[21] then the difference in the ΔV's between $(\text{P-}V)^0$ and $(\text{P-}V)^-$, namely 4.8 Å^3, should, to a good approximation, correspond to the volume relaxation associated with the capture of an electron by the P-V center. The sign of the effect implies inward relaxation of ~ 4.8 Å^3 on electron capture and *outward* relaxation of the same amount on subsequent emission. This conclusion is in accord with the present results in Fig. 9. The result from the annealing study is depicted by the dotted line in Fig. 9, and it is close to the upper bound on ΔV_n determined from the present study. Although we recognize that the above interpretation of the annealing data is based on a strong assumption which at present cannot be tested, it is felt thta the close agreement between the ΔV_n's is not fortuitous.

2. *The $E_c - 0.23$ divacancy and $E_c - 0.40$ levels*

Figure 11 shows the ΔV_n results for the $E_c - 0.23$ and $E_c - 0.40$ levels. Again, we show two bounds for the ΔV_n's which are essentially independent of T. The average of the two bounds in each case is $\Delta V_n = -0.6$ Å^3 (emitted electron) for the $E_c - 0.23$ level and $+4.3$ Å^3/(emitted electron) for the $E_c - 0.40$ level. The latter ΔV_n is of the same sign and magnitude as that for the P-V center discussed above. These results imply a small *inward (outward)* relaxation on electron emission (capture) for the $E_c - 0.23$ level and a relatively large *outward (inward)* relaxation on electron emission (capture) for the $E_c - 0.40$ level.

Because of the highly asymmetric nature of the divacancy, it would be difficult to interpret the above ΔV_n of the $E_c - 0.23$ in terms of changes in near-neighbor distances. We thus restrict our considerations to the sign and magnitude of the total breathing-mode volume relax-

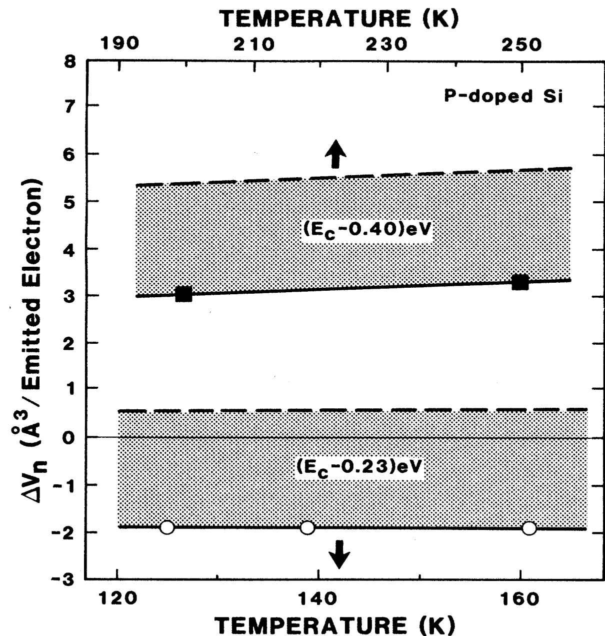

FIG. 11. Breathing-mode volume relaxations accompanying electron emission from the $E_c - 0.23$ divacancy and $E_c - 0.40$ levels in Si. The upper and lower bounds for each level are discussed in the text.

ation, ΔV_n. As discussed below, the sign of ΔV is consistent with the accepted model for the divacancy. As for the $E_c - 0.40$ level, it was speculated above that the level may be associated with one of the configurations of the P-C_i pair defect; however, this assignment is by no means certain. The positive sign of ΔV_n on electron emission for this level is indicative of bondinglike character. On electron capture, the Si near neighbors relax inward to strengthen their bonds to the defect. On electron emission, the opposite effect (outward relaxation) can be expected, as observed. The pressure results also suggest that with increasing pressure the level falls deeper into the band gap, which is also expected for a bondinglike level.

E. Model for the P-V pair defect

The present pressure results are consistent with and support the generally accepted model for the P-V pair or Si E center. This model[10] is based on EPR data and, as already noted, leads to the conclusion that the P-V center consists of a substitutional P and a Si vacancy. According to Watkins and Corbett,[10] one can picture the formation of this center as depicted schematically in Fig. 10.

Starting with a Si vacancy (V), there are four broken bonds around V, one each for the four atoms surrounding it; i.e., for the isolated V there are four degenerate one-electron orbitals associated with the four nearest-neighbor Si dangling bonds. Replacing atom c by a P is equivalent to adding an extra positive charge at this site.

This partially removes the degeneracy, and orbital c is lowered in energy by an amount equivalent to the Coulomb energy.

In the neutral charge state five electrons are accommodated in these orbitals: two electrons are paired in the c orbital, and the remaining three electrons are in the a, b, and d sets of orbitals. Because of the degeneracy associated with the partially filled a, b, and d orbitals, a spontaneous Jahn-Teller distortion sets in to remove the degeneracy. Two of the Si atoms, a and d in the figure, pull together to form an electron-pair bond, and the remaining unpaired electron is primarily located in a dangling bond orbital on the remaining Si atom b.[10] Since the orbital of this atom is not involved in bonding to other atoms across from the vacancy, we would expect that atom b would be pulled away from the vacancy by the strong bonds to its three remaining near Si neighbors (i.e., the deficiency in the number of valence electrons forces atom b to relax outward).

The capture of an electron makes the center negatively charged. As this electron is added to an electron-deficient orbital, it increases the covalent character of the orbital on the b atom, and the atom relaxes back toward its normal position (weakening its bonding to its three-Si near neighbors).

Another way of looking at this is that the extra electron, which is of a symmetry, pairs with the existing electron on atom b in a bonding orbital further stabilizing the configuration. Pressure further stabilizes this paired bonding configuration, and the energy level E_T falls deeper in the gap as observed. On emission we, of course, expect the opposite effect, i.e., an outward relaxation, and this is what we find in the present work.

In summary, the present results are in good qualitative agreement with, and lend support to, the model for the P-V center. Specifically, pressure forces the level deeper in the gap consistent with its bonding character and its ability to mix with other orbitals (because of the level's a symmetry); the lattice relaxes outward (inward) on emission (capture); and the relaxation is relatively large.

F. Model for the Si divacancy

As already noted, there is a body of evidence from DLTS measurements[12,13] which indicates that the $E_c - 0.23$ level is associated with the $2-/-$ charge state of the divacancy. Although some uncertainties remain about this assignment, the pressure results are consistent with the generally accepted model for the divacancy.

On the basis of detailed EPR results, Watkins and Corbett[11] proposed the simplified model for the divacancy shown in Fig. 12. The two vacancies (V-V) are on two adjacent sites c and c'. The formation of V-V initially results in six broken bonds, one each for the six neighboring atoms a, b, d, a', b', and d'. The undistorted structure would have D_{3d} symmetry, the six electrons from the six broken bonds occupying the a_{1g}, a_{1u}, and e_u orbitals as shown: the first four electrons are paired off into a_{1g} and a_{1u} and the remaining two electrons go into the e_u doublet partially filling it. This would represent the neutral charge state, $(V\text{-}V)^0$, of the divacancy. However, because of the degeneracy associated with the partially filled e_u orbitals, a Jahn-Teller distortion occurs, lowering the symmetry to C_{2h}. This distortion, one manifestation of which is the formation of bent pair bonds between atoms a and d and a' and d', allows strong mixing to occur between the a_g levels and between the b_u levels. The resulting molecular orbitals are linear combinations of one-electron orbitals which reflect primarily the pair bonding and the extended orbitals between atoms b and b' (with little admixture among the other atomic orbitals). Two EPR spectra of the divacancy are observed:[11] one corresponding to only one unpaired electron in the extended orbital between b and b'—this is the singly positive charge state, $(V\text{-}V)^+$, of the divacancy, and the other corresponds to the singly negative charge state, (V-

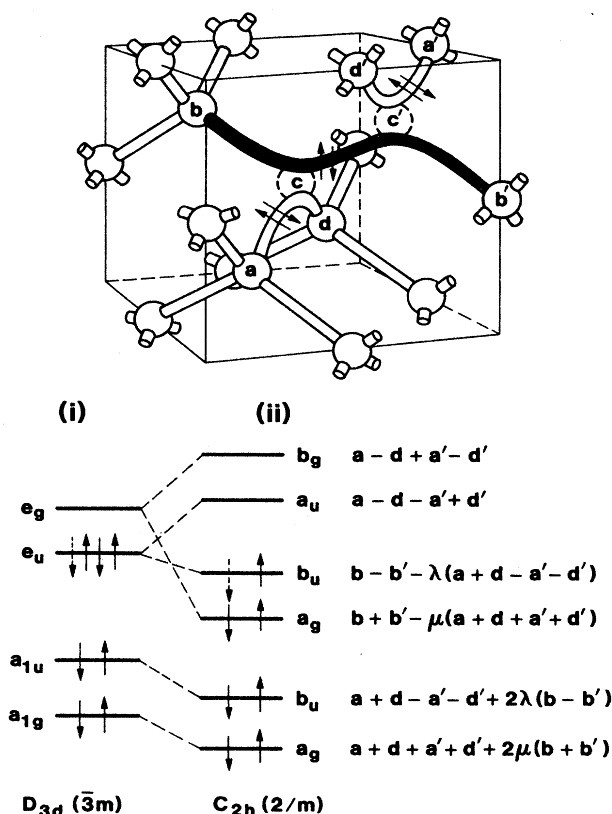

FIG. 12. Top: Model for the structure of the Jahn-Teller-distorted divacancy in Si showing the pair bonds between a and d and a' and d' and the extended bond between atoms b and b'. Bottom: Simplified molecular-orbital model of the electronic structure of the negatively charged divacancy, $(V\text{-}V)^-$, before (i) and after (ii) the Jahn-Teller distortion. In (ii) the linear combination of one-electron orbitals which form the various molecular orbitals are given. A captured electron (dashed arrow) to form $(V\text{-}V)^{2-}$ goes into the antibondinglike b_u molecular orbital. The $E_c - 0.23$ level studied in the present work is associated with the $2-/-$ transition. (After Watkins and Corbett, Ref. 11).

$V)^-$, with three electrons in the orbital between b and b'.

Starting with the neutral charge state $(V\text{-}V)^0$, a captured electron goes unpaired into the antibondinglike state b_u (which is made up of linear combination of atomic orbitals b-b and little admixture from the other orbitals represented by the λ term).[24] This is the $(V\text{-}V)^-$ state of the divacancy. On further electron capture to form $(V\text{-}V)^{2-}$, the second captured electron also goes into the same antibonding b_u state pairing with the first electron. In going from $(V\text{-}V)^-$ to $(V\text{-}V)^{2-}$ the electron is captured into an already negatively charged state which is also antibonding in character. Such a capture process can be expected to lead *outward* relaxation of the near-neighbor Si atoms. On subsequent electron emission from $(V\text{-}V)^{2-}$, the opposite effect obtains, i.e., *inward* relaxation, as we deduce from the present experiments. The magnitude of the relaxation is, however, relatively small. This may simply be related to the asymmetric and extended nature of the divacancy. Additionally, since the V-V $2-/-$ level is antibonding in character, compressing the lattice should force the level higher in the gap. This is also what we observe experimentally. Thus it is seen that the pressure results are consistent with the model.

It was noted earlier in the paper that the divacancy has a second acceptor level at $E_c - 0.41$ corresponding to the $-/0$ state. We did not study the pressure dependence of this level; however, on the basis of the above model, we can qualitatively predict what should be observed. Again in this case, electron capture will be into the antibonding b_u state, and this should lead to *outward* relaxation *(inward* on subsequent emission) and the $-/0$ level should also move higher in the gap with pressure. We hope to confirm these predictions experimentally in a future study.

IV. CONCLUDING REMARKS

In this paper we have presented and discussed the combined effects of temperature and hydrostatic pressure on the deep levels of two important vacancy-related defects in Si, the P-V pair acceptor at $E_c - 0.44$ and the $2-/-$ V-V acceptor at $E_c - 0.23$, and on a third level of uncertain origin at $E_c - 0.40$. The results and conclusions can be summarized as follows.

(i) For the P-V acceptor, the electron thermal emission rate (e_n) decreases with pressure at constant temperature, and the electron capture cross section is essentially independent of temperature and pressure. Analysis of these results leads to the conclusion that the level falls deeper into the band gap with pressure, and that the breathing-mode lattice relaxation is outward, i.e., expansion, on electron emission. The opposite relaxation should obtain on electron capture. These findings are consistent with Watkins and Corbett's model for this defect and with the bondinglike nature of its deep level.

(ii) The results for the $E_c - 0.40$ level are qualitatively similar to those for the P-V pair acceptor.

(iii) The results for the $2-/-$ V-V acceptor are, however, qualitatively different. In this case, e_n increases with pressure while σ_n is again essentially independent of temperature and pressure. With pressure this level moves higher in the gap, and the breathing-mode volume relaxation is inward (outward) on electron emission (capture). These results are also consistent with Watkins and Corbett's model for the V-V defect and with the antibonding nature of its $2-/-$ level.

The present results, when combined with earlier results[16] on other deep levels in Si, reveal the following generalization. Those deep levels whose electronic orbitals are bondinglike in character move lower in the band gap on lattice compression, and the lattice relaxes inward (outward) on electron capture (emission) by such levels. Deep levels whose electronic orbitals are antibondinglike in character, on the other hand, exhibit the opposite effects. This generalization is consistent with intuitive expectations, and the present results quantify the effects. A level can be expected to move lower in the band gap as a reflection of its more stable bonding configuration at high pressure. Capture of an electron by such a level should also strengthen the bonding of the defect (or impurity) to its Si neighbors, and this should lead to inward relaxation of these neighbors. The opposite effects follow for antibonding levels.

Finally, we note that the main uncertainty in the quantitative values of the volume relaxations given in the paper derives from the lack of definitive values for the hydrostatic deformation potentials of the two band edges, E_c and E_v.[16] In addition to their needs in the present work, these deformation potentials are important to the understanding of other pressure effects as well as some fundamental properties (e.g., acoustic-phonon scattering) of Si.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the excellent technical assistance of L. V. Hansen and technical discussions with K. L. Brower. This work was performed at Sandia National Laboratories and is supported by the U.S. Department of Energy under Contract No. DE-AC04-76DP00789.

[1]G D. Watkins, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 147.

[2]C. E. Barnes and G. A. Samara, Appl. Phys. Lett. **48**, 934 (1986).

[3]L. W. Song, B. W. Benson, and G. D. Watkins, Phys. Rev. B **33**, 1452 (1986); Appl. Phys. Lett. **51**, 1155 (1987).

[4]A. Chantre, J. L. Benton, M. T. Asom, and L. C. Kimerling, in *Defects in Semiconductors,* edited by H. J. von Bardeleben (Trans Tech, Aedermannsdorf, Switzerland, 1986), p. 1111.

[5]M. T. Asom, J. L. Benton, R. Sauer, and L. C. Kimerling, Appl. Phys. Lett. **51**, 256 (1987); Mater. Res. Soc. Symp. Proc. **104**, 85 (1988).

[6]G. E. Jellison, Jr., J. Appl. Phys. **53**, 5715 (1982).

[7]G. A. Samara and C. E. Barnes, Phys. Rev. B **35**, 7575 (1987),

and references therein.

[8]G. A. Samara, Phys. Rev. B **36**, 4841 (1987).

[9]C. E. Barnes and G. A. Samara, Appl. Phys. Lett. **43**, 677 (1988).

[10]G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

[11]G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

[12]See, e.g., B. G. Svensson and M. Willander, J. Appl. Phys. **62**, 2758 (1987), and references therein.

[13]A. D. Evwaraye and E. Sun, J. Appl. Phys. **47**, 3776 (1976).

[14]C. T. Sah, L. Forbes, L. L. Rosier, and A. F. Tasch, Jr., Solid-State Electron. **13**, 759 (1970).

[15]D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).

[16]G. A. Samara, Phys. Rev. B **39**, 11 001 (1989).

[17]W. Paul and D. M. Warschauer, in *Solids Under Pressure,* edited by W. Paul and D. M. Warschauer (McGraw-Hill, New York, 1963), Chap. 8, p. 179.

[18]See, e.g., K. Wünstel, O. Kumagai, P. Wagner, and W. Jantsch, Appl. Phys. A **27**, 251 (1982), and references therein.

[19]V. L. Bonch-Bruereich and E. G. Landsberg, Phys. Status Solidi **29**, 9 (1968).

[20]C. E. Barnes and G. A. Samara, Mater. Res. Soc. Symp. Proc. **46**, 471 (1985).

[21]G. A. Samara, Phys. Rev. B **37**, 8523 (1988).

[22]See, e.g., D. D. Nolte, W. Walukiswicz, and E. E. Haller, Phys. Rev. B **38**, 6316 (1988).

[23]G. A. Samara and C. E. Barnes, Phys. Rev. B **38**, 6318 (1988).

[24]There is some disagreement about the relative energy ordering of the b_u and a_g levels, with model calculations showing b_u below a_g [see, e.g., P. Pecheur and G. Toussant, in Ref. 4, p. 43, and M. J. Kirton, P. W. Banks, Lu Da Lian, and M. Jaros, J. Phys. C **17**, 2487 (1984)]. In either case, however, the captured electron goes into an antibonding state, which is the important point for our present considerations.