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Pressure dependence of deep electronic levels in semiconductors: The oxygen-vacancy pair (or A center) in silicon

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A study of the pressure and temperature dependences of the electron thermal emission rate and capture cross section for the oxygen-vacancy (O-V) pair (or A center) deep level in n-type silicon is presented. The results allow characterization of the three important thermodynamic parameters, namely the Gibbs free energy, the enthalpy, and the entropy associated with electron emission from this level and their pressure dependences. Analysis of the results leads to the following highlights of the work. (1) There is a large breathing-mode lattice relaxation accompanying electron emission. The sign of this effect implies that the lattice relaxes inward (i.e., contracts) upon emission and outward (i.e., expands) upon capture. The sign is in agreement with the prediction of a model for the O-V pair defect based on EPR results but, as far as we know, the present results provide the first and only quantitative measure of this relaxation. (2) The energy of this level is not pinned to either the conduction- or valence-band edges. The level moves higher in the gap with pressure consistent with its expected antibonding character. (3) The electron-capture cross section is found to be essentially temperature and pressure independent. It is suggested that this result can be understood in terms of nonradiative electron capture by multiphonon emission.

I. INTRODUCTION

In this paper we present and discuss the results of an experimental study of the effects of hydrostatic pressure and temperature on the properties of the deep electronic level associated with the oxygen-vacancy (O-V) pair (or the A center) in silicon (Si). This center, which produces an acceptor level at ~ 0.17 eV below the conduction-band edge, is a major defect produced by high-energy particle or photon irradiation of Si crystals grown by pulling from the melt. Oxygen is generally found in concentrations up to $\sim 10^{18}$ cm^{-3} in pulled Si. Early electron-spin resonance and infrared studies[1,2] concluded that this center is a single oxygen atom in a Si lattice vacancy which is presumably formed when a mobile vacancy is trapped by an interstitial oxygen. On the basis of these studies a model was proposed[1,2] for this center, which remains as the generally accepted model.

Because deep centers are characterized by strongly localized, lattice-perturbing potentials, lattice relaxation can be expected to occur in the vicinity of such centers, and additional relaxations would accompany electron or hole emission and capture processes at these centers. The existence of these latter relaxations is a much discussed and debated topic,[3(a)] but apparently there are no experimental measurements of them, and it has been only recently that theory has begun to address them in a detailed way.[3(b)] In the case of the O-V pair, the atomic model suggests the presence of relatively large relaxations. Knowledge of these relaxations for the different charge states of this center are important to the full understanding of the nature of the center.

We have recently proposed a method for evaluating volume (or breathing mode) lattice relaxations accompanying the emission or capture of charge carriers at deep centers based on measuring the hydrostatic pressure dependence of the carrier's thermal emission rate and capture cross section.[4] The method was demonstrated for the deep gold acceptor and for the O-V pair acceptor in Si. Only a brief account of the O-V pair acceptor results was reported in Ref. 4. In the present paper we present a more-detailed account of the results of the pressure and temperature dependences of the electronic properties of this center. The results yield a detailed evaluation of the thermodynamic properties (Gibbs free energy, enthalpy, and entropy) and their pressure dependences as well as new insights into the nature of this important center. The calculated lattice volume relaxation is found to be relatively large, and its sign is qualitatively consistent with what is expected on the basis of the existing model.

The experimental details are given in Sec. II. Section III provides a brief summary of the necessary theoretical background. This is followed by presentation and discussion of the results in Sec. IV and a few concluding remarks in Sec. V.

II. EXPERIMENTAL DETAILS

The O-V pair defect was studied by transient capacitance[5] and deep-level transient spectroscopy[6] (DLTS) techniques, the measurements being done in the high-field depletion region of reverse-biased p^+-n junction diodes. The diodes were fabricated from Czochralski-grown Si which was ion-implanted and annealed. The n region of the diodes was doped with phosphorous at 4×10^{15} cm^{-3}, and the p region was doped with boron at 5×10^{18} cm^{-3}. The starting Si wafers contained a small uniform gold concentration at $\sim 1\times10^{14}$ cm^{-3}. The gold DLTS peaks were far removed from the A-center

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peaks and did not present any apparent difficulty. The O-V pair defect was introduced by γ irradiation to a total dose of 5×10^8 rads. The active junction area was 9.2×10^{-3} cm^2.

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, emission energy, and their pressure dependences. The effects of electric field 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 as a function of the length of the trap-filling pulse.[7]

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 ~300 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.

III. THEORETICAL BACKGROUND

In the present work we investigated electron emission and capture by the O-V pair acceptor level. General detailed balance considerations relating thermal emission and capture rates for deep levels yield the following expression for the thermal electron emission rate[8] e_n:

$$e_n=\sigma_n\langle v_n\rangle N_c\exp(-\Delta G_n/kT)\ , \tag{1}$$

where σ_n is the electron capture cross section, $\langle v_n\rangle$ is the average electron thermal velocity, N_c is the effective density of states in the conduction band, and ΔG_n is the change in the Gibbs free energy which accompanies the emission of the electron from the deep level. As the Gibbs free energy is defined by

$$G=H-TS\ , \tag{2}$$

where H is the enthalpy and S is the entropy, Eq. (1) can be rewritten as

$$e_n=\sigma_n\langle v_n\rangle N_c\exp(\Delta S_n/k)\exp(-\Delta H_n/kT)\ . \tag{3}$$

In Eq. (3), ΔS_n and ΔH_n are the total entropy and enthalpy changes accompanying electron emission. ΔS_n is the sum of the changes in entropy due to electronic degeneracy and due to atomic vibrational changes.[8]

In interpreting the temperature and pressure dependences of e_n, we note the following: For the A center in Si we find that, as we shall see later, σ_n is pressure independent. The thermal velocity is given by $\langle v_n\rangle=(3kT/m_n^*)^{1/2}$, where m_n^* is the electron effective mass. The density of states N_c is given by $N_c=2(m_n^*kT/2\pi h^2)^{3/2}M_c$, where M_c is the number of equivalent minima in the conduction band. Thus, the product $\langle v_n\rangle N_c$ is proportional to $m_n^*T^2$. The pressure dependence of m_n^* in Si is very weak, $(\partial\ln m_n^*/\partial P)$ being on the order of 10^{-3} per kbar.[9,10] We shall see later that this effect is negligibly small compared to the pressure dependence of e_n. Thus, to a good approximation for the present case, we can neglect the small pressure dependence of the product $\langle v_n\rangle N_c$.

On the basis of the above considerations we thus see that the slope of a $\ln(e_nT^{-2})$ versus T^{-1} Arrhenius plot is simply ΔH_n, and that such plots at different pressures yield the pressure dependence of ΔH_n. On the other hand, measurements of e_n versus pressure P at constant T yield the pressure dependence on ΔG_n since from Eq. (1) and the above considerations we have

$$\left[\frac{\partial\ln e_n}{\partial P}\right]_T=-(kT)^{-1}\left[\frac{\partial\Delta G_n}{\partial P}\right]_T\ . \tag{4}$$

Knowing the pressure dependences of ΔG_n and ΔH_n allows determination of the pressure dependence of ΔS_n, since from Eq. (2) we see that

$$\left[\frac{\partial\Delta G_n}{\partial P}\right]_T=\left[\frac{\partial\Delta H_n}{\partial P}\right]_T-T\left[\frac{\partial\Delta S_n}{\partial P}\right]_T\ . \tag{5}$$

From the well-known thermodynamic relation

$$dG=VdP-SdT\ , \tag{6}$$

it is readily seen that

$$\left[\frac{\partial\Delta G_n}{\partial P}\right]_T=\Delta V_n\ , \tag{7}$$

i.e., the isothermal pressure dependence of ΔG_n measures a volume change, which we represent by ΔV_n. We have conjectured that this thermodynamic volume change is the volume change, or lattice volume relaxation of the defect which accompanies electron emission.[4] The present results should thus provide a direct measure of this relaxation at the O-V pair center.

The above arguments follow from straightforward thermodynamic considerations and the use of the well-known detailed balance result, Eq. (1). In interpreting experimental results, however, there is an additional consideration.[9] For the O-V acceptor the measured electron emission is from the deep acceptor level E_T to the conduction-band edge E_c, and the pressure dependence of e_n is determined by the isothermal pressure dependence of the Gibbs free-energy difference between the two different charge states of the level, i.e., before and after emission. In the experiment, E_c is the reference energy state relative to which the change in the energy of the deep level is measured. However, since the energy gap of Si changes with pressure, this reference energy state is not fixed, and it is necessary to consider its change in the analysis of the data.[9(a),9(b)]

In this regard, it is helpful to consider two limiting cases.

Case 1. The total pressure-induced shift of the gap is taken up by a shift in the valence-band edge, E_v, with E_c remaining fixed. In this case e_n (and thereby ΔG_n) is not influenced by the pressure shift of the gap. This is the case treated in Ref. 4.

Case 2. The total pressure-induced shift of the gap is taken up by a shift in E_c with E_v remaining fixed. Here the full pressure shift of the gap contributes to the pressure dependence of e_n, and, in order to determine the *intrinsic* pressure dependence of ΔG_n of the deep level, it is necessary to subtract the known shift of the Gibbs free energy of the Si gap from the total experimentally-determined pressure derivative $(\partial \Delta G/\partial P)_T$. The shift of the gap is, to within a small but unknown temperature-dependent correction, $(\partial \Delta G/\partial P)_{T,\mathrm{gap}} = -1.5$ meV/kbar.[10]

By intrinsic pressure dependences of ΔG_n and other thermodynamic properties, we mean here the pressure dependences of these properties in the absence of any contribution from the shift of the gap. For emphasis, in what follows we shall drop the subscript n from the pressure derivatives of the thermodynamic properties when we refer to total experimentally-determined pressure effects which include contributions from the shift of the gap. Derivatives with the subscript n refer to the intrinsic properties of the deep level.

For the O-V acceptor, case 1 above leads to an upper bound on the magnitudes of the intrinsic pressure derivatives and case 2 leads to a lower bound. The exact values can be determined from knowledge of how much the individual band edges contribute to the shift of the gap. In the absence of such knowledge, it is reasonable to expect that the intrinsic values should lie between the two bounds (half way in a simplistic tight-binding picture).

IV. RESULTS AND DISCUSSION

A. Electron thermal emission rate and energy

We find that the electron thermal emission rate e_n for the O-V pair acceptor is very strongly pressure dependent. This can be easily deduced both from the typical DLTS spectra shown in Fig. 1 and from capacitance transients measured as a function of time after the application of reverse bias. Figure 2 shows typical normalized transient data at different temperatures and pressures displayed on a semilogarithmic plot. The linearity of such plots attests to the exponential decay of the capacitance. The slope of each straight line in the figure yields e_n at the indicated temperature and pressure conditions.

It is found that e_n increases logarithmically with pressure. The slope, $(\partial \ln e_n/\partial P)_T$, decreases from 0.57 ± 0.02 kbar^{-1} at 77 K to 0.42 ± 0.03 kbar^{-1} at 100 K. This temperature dependence is shown for all the present data in Fig. 3. Use of the slopes $(\partial \ln e_n/\partial P)_T$ in Eq. (4) yields the values of $(\partial \Delta G/\partial P)_T$ also shown in Fig. 3. This quantity, which represents the total pressure dependence of ΔG including the contribution from the shift of the gap, decreases slightly in magnitude from $\sim -3.7 \pm 0.2$ meV kbar^{-1} at 77 K to $\sim -3.5 \pm 0.3$ meV kbar^{-1} at 100 K.

Keller[11(a)] has recently reported the pressure dependence of e_n for the O-V pair at 80 K. His results yield[11(b)] $(\partial \ln e_n/\partial P)_T \approx 0.40$ kbar^{-1} and

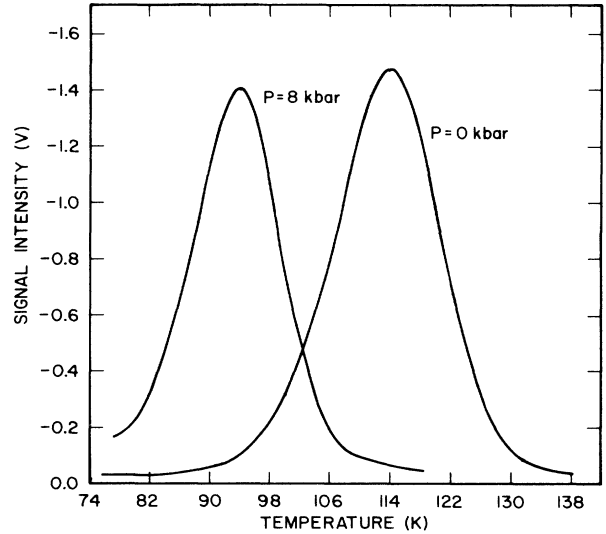

FIG. 1. The pressure dependence of the DLTS spectrum of electron emission from the O-V pair deep level in silicon. The rate window is 1.28×10^4 s^{-1} and the bias voltage is -4 V.

$(\partial \Delta G/\partial P)_T = -2.8$ meV kbar^{-1}, both quantities considerably smaller than our results in Fig. 3. We believe that the difference is most likely due to the fact that in Keller's sample the O-V pair was produced by 350-keV ^{30}Si ion implantation. This implantation produces many complex defects, some in concentrations larger than that of the O-V pair. The complicated nature of these defects

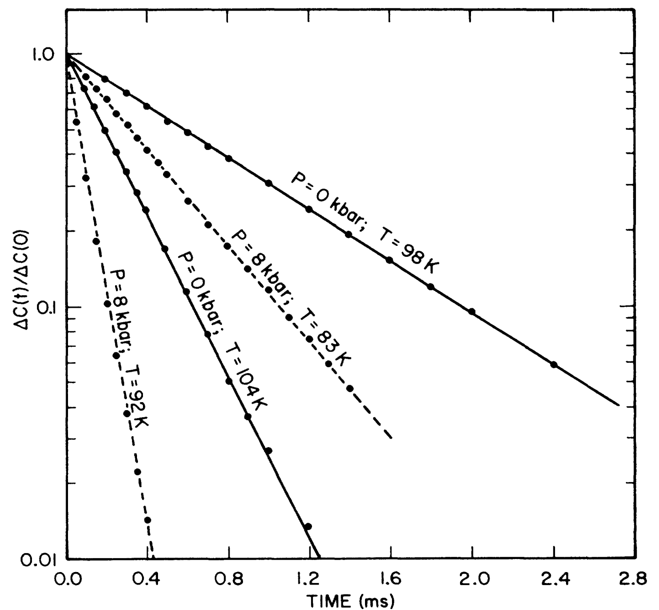

FIG. 2. Normalized capacitance transients for electron emission from the O-V pair deep level in silicon measured at different pressures and temperatures. The slope of each line yields the emission rate which is seen to be strongly temperature and pressure dependent.

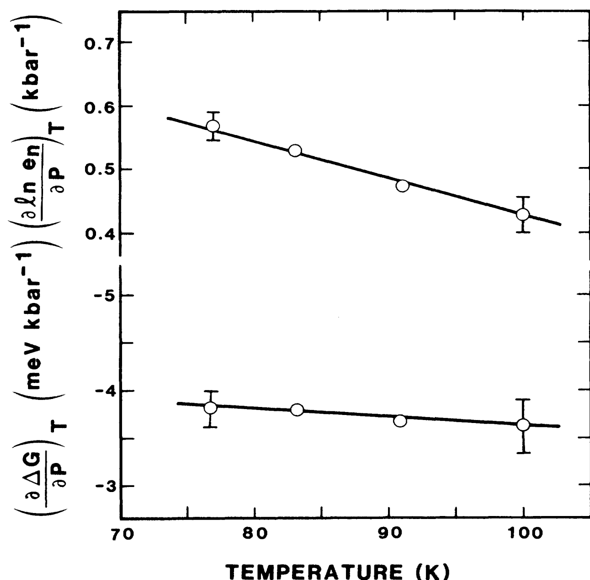

FIG. 3. Temperature dependences of the logarithmic pressure derivative of the electron emission rate (e_n) and of the pressure derivative of the Gibbs free-energy change (ΔG) for the O-V pair deep level in silicon.

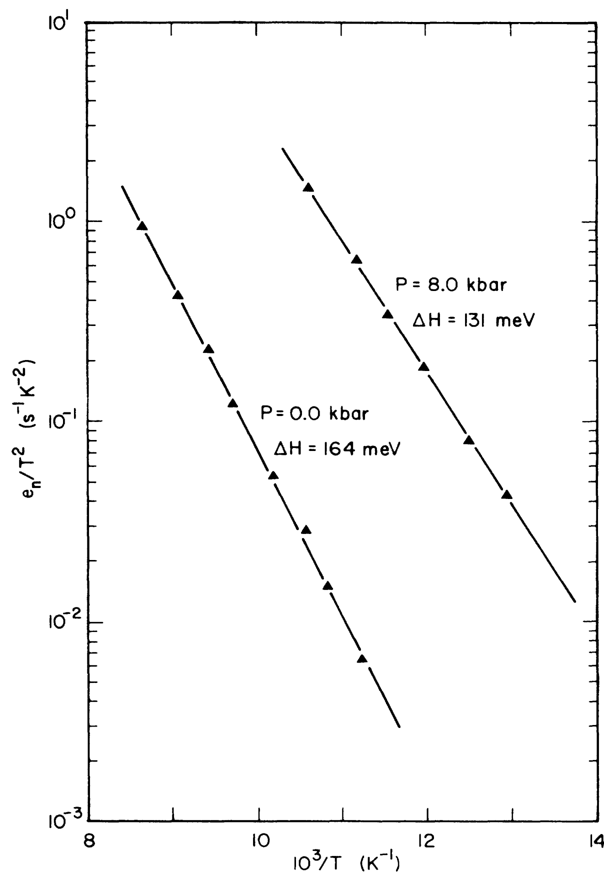

FIG. 4. Arrhenius plot of the temperature dependence of the electron thermal emission rate from the O-G pair deep level in silicon at 0 and 8 kbar. Note the large decrease in the activation energy (enthalpy) ΔH with pressure.

is reflected in the resulting DLTS spectrum (Fig. 5 of Ref. 11), which also shows a large asymmetry in the O-V acceptor peak. This asymmetry (absent in our data in Fig. 1) and the quantitative disagreement with our results cited above are likely due to interaction between the O-V defect and other defects in Keller's sample.

The pressure dependence of ΔH was determined from a series of $\log_{10}(e_n T^{-2})$ versus T^{-1} Arrhenius plots each measured at a fixed pressure. Typical results are shown in Fig. 4. The slope of the 1 bar ($P=0$) data yields $\Delta H_n = 164$ meV in good agreement with earlier work.[1,2,11] We equate this enthalpy with the ionization energy of the level, $E_c - E_T$, where E_T is the deep-level (trap) energy. The results in Fig. 4 show that ΔH decreases significantly with pressure, and it is this decrease which is responsible for much of the increase in e_n with pressure.

The pressure dependence of ΔH, or $\Delta E = E_c - E_T$, which also includes a contribution from the shift of the gap, is shown in Fig. 5. Over the 8-kbar range of the data, the decrease in ΔE is linear with a slope of -3.9 ± 0.4 meV kbar^{-1}, implying that E_T *moves closer* to E_c at a rate of 3.9 meV per kbar. For comparison we show by the dashed line in the inset in Fig. 5 the shift of the band-gap energy, E_g, with pressure, where the slope is[10] -1.5 meV kbar^{-1}. From the results in Fig. 5 we deduce that E_T *moves away* from the valence-band edge E_v at a rate of 2.4 meV kbar^{-1}. This is indicated schematically by the inset in Fig. 5.

These results clearly show that the O-V pair deep acceptor level is not pinned to either the valence- or conduction-band edges. Intuitively this is a satisfying result since one does not expect the wave functions describing a deep level to consist mainly of wave functions from a single valence or conduction band. The fact

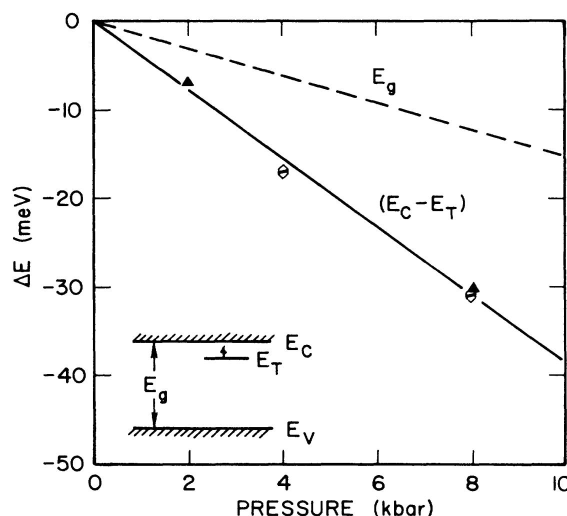

FIG. 5. Pressure dependence of the activation energy, $E_c - E_T$ (or ΔH), for the O-V pair deep level in silicon compared with that of the energy gap, E_g. The inset depicts the fact that E_T moves closer to E_c (and farther from E_v) with pressure, i.e., E_T is not pinned to either E_c or E_v.

that a deep level has a strong localized (in real space) potential implies that its wave functions are delocalized in momentum space, and the level thus couples to a variety of momentum vectors or bands.

The fact that E_T moves away from E_v, i.e., moves higher in the gap, with pressure suggests that this acceptor level is determined by antibonding states in the gap. This is consistent with the model for the O-V defect which will be discussed below.

B. Electron-capture cross section

The capture cross section was determined from the initial capacitance amplitude after reverse bias, $\Delta C(0,\delta)$, as a function of the filling pulse duration δ. It can be shown[7] that $\Delta C(0,\delta)$ is given by

$$\Delta C(0,\delta) \propto \Delta C(0,\delta \rightarrow \infty)[1-\exp(-n\sigma_n\langle v_n\rangle\delta)] , \quad (8)$$

where n is the free-carrier density and $\Delta C(0,\delta\rightarrow\infty)$ is the saturated capacitance amplitude obtained at sufficiently long pulse duration. It is thus seen that a plot of $\ln[1-\Delta C(0,\delta)/\Delta C(0,\delta\rightarrow\infty)]$ versus δ should yield, over a certain range of δ, a straight line whose slope is $-n\langle v_n\rangle\sigma_n$. Some data for the O-$V$ acceptor are shown in Fig. 6. From the slope and the known values of n $(=3.6\times10^{15}\ \mathrm{cm}^{-3})$ and $\langle v_n\rangle$ $(=1.09\times10^{7}\ \mathrm{cm\,s}^{-1}$ at 90 K), we obtain $\sigma_n \approx 2.4\times10^{-16}\ \mathrm{cm}^2$ at 90 K.

It is seen that within the scatter of the data the slope in Fig. 6 is independent of temperature and pressure. Since $\langle v_n\rangle \propto T^{1/2}$, a weak T dependence, the T independence of the slope in Fig. 6 implies that σ_n is very weakly T dependent also. As the pressure dependences of the free-carrier density n is negligible and that of $\langle v_n\rangle$ is very weak, as discussed above, the results in Fig. 6 show that σ_n is independent of pressure, i.e., $(\partial\ln\sigma_n/\partial P)\approx 0$. We emphasize that while σ_n is independent of pressure for the O-V pair, this is not always the case.[12]

The lack of appreciable temperature and pressure dependences of σ_n raises some interesting questions about the mechanism responsible for nonradiative electron capture at this deep acceptor level. The situation here is very similar to that recently discussed for the deep gold acceptor in Si.[9] In that case it was concluded that electron capture occurs by a multiphonon emission (MPE) process, and we believe that the same process is probably operable for the O-V pair acceptor as well. Theoretical expressions for the capture rate (and hence σ) in the MPE process have been derived in both the classical[13] (i.e., high-temperature) and quantum regimes.[14,15] Whereas, through the work of Henry and Lang,[13] many researchers have come to identify MPE with a thermally-activated cross section, we emphasize that this behavior is valid only in the high-T classical regime. The observed temperature independence of σ_n for the O-V pair acceptor is a natural consequence of the MPE theory in the low-temperature regime (we note that the Debye temperature of Si is $\sim$625 K).[14,15] The absence of an appreciable pressure dependence of σ_n is most likely due to cancelling (and presumably small) pressure effects among the various parameters involved in the expression for σ_n.[9]

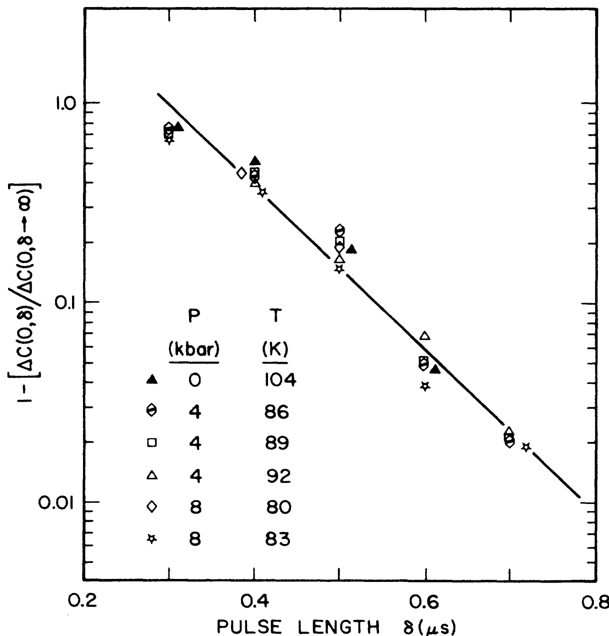

FIG. 6. Normalized initial capacitance amplitude after reverse bias as a function of filling pulse duration δ for the O-V pair deep level in silicon measured at different pressures and temperatures.

C. The entropy factor

The entropy change ΔS_n, or the entropy factor $\exp(\Delta S_n/k)$, is one of the most important characteristic properties of a deep level. From the above data and Eq. (3) we can calculate the total entropy change accompanying electron emission for the O-V pair acceptor deep level. Thus, e.g., at $T=90$ K we find $\Delta S_n=2.1k$. This value was obtained from Eq. (3) using the following values of the various parameters; $e_n=71.3\ \mathrm{s}^{-1}$, $v_n=1.09\times10^{7}\ \mathrm{cm\,s}^{-1}$, $\sigma_n=2.4\times10^{-16}\ \mathrm{cm}^2$, $N_c=5.1\times10^{18}\ \mathrm{cm}^{-3}$, $m_n^*=3.15\times10^{-28}$ g, and $\Delta H_n=0.164$ eV. We note that this ΔS_n, which represents the sum of changes in entropy due to electronic degeneracy and due to atomic vibrational changes, is quite large.

Going back to Eq. (5), the total pressure dependences of ΔG and ΔH allow a determination of the total pressure dependence of ΔS. We find that ΔS *decreases* with pressure, and the magnitude of the slope $(\partial\Delta S/\partial P)_T$ *increases* from $\sim -2\times10^{-3}\ \mathrm{meV\,kbar^{-1}\,K^{-1}}$ at 77 K to $\sim -3.9\times10^{-3}\ \mathrm{meV\,kbar^{-1}\,K^{-1}}$ at $\sim$100 K (Fig. 3). In considering these numbers, it should be emphasized that the quantity $T(\partial\Delta S/\partial P)_T$ in Eq. (5) is determined by the difference between two relatively large and nearly equal numbers, namely the pressure derivatives of ΔG and ΔH. Thus, the absolute magnitude of $(\partial\Delta S/\partial P)_T$ may involve considerable uncertainty; however, the qualitative effects, namely the decrease of ΔS with pressure and the increase in the magnitude of $(\partial\Delta S/\partial P)_T$ with temperature are well established.

Since the intrinsic ΔS_n associated with the emission process is more than twice as large as the entropy change associated with excitation across the gap, ΔS_{cv} [$2.1k$ versus $1k$ (Ref. 16) at 90 K], and because of the deformed nature of the lattice around the defect, we presume that much of the above pressure dependence of ΔS is due to the intrinsic pressure dependence of the entropy change accompanying emission, i.e., $(\partial \Delta S_n / \partial P)_T$. It is also reasonable to assume that the electronic degeneracy factor does not change appreciably with pressure, and thus the indicated change in ΔS with pressure reflects mostly the pressure dependence of the vibrational part of ΔS_n. A decrease of ΔS_n with pressure can be qualitatively understood on this basis, since the vibrational contribution can be expected to get smaller as the local environment of the defect becomes stiffer with compression. A large vibrational entropy is also consistent with a relatively large lattice relaxation (see next section) which can also be expected to become smaller with compression. An increase in the magnitude of $(\partial \Delta S_n / \partial P)_T$ with increasing T can also be qualitatively understood on a similar argument, namely, increasing T softens the lattice and thereby makes the effect of compression more pronounced.

D. Lattice relaxation accompanying electron emission

As already noted, the isothermal pressure dependence of ΔG_n provides a direct measure of the volume relaxation ΔV_n [Eq. (7)]. Using the pressure derivatives of ΔG in Fig. 3, we obtain the upper bound for the values of ΔV_n as shown in Fig. 7. This corresponds to case 1 discussed in Sec. III. The lower bound on ΔV_n, which corresponds to case 2, is represented by the dashed line in Fig. 7. We note that ΔV_n is negative implying that the lattice relaxes *inward* (i.e., contracts) upon electron emission from the O-V acceptor level. We expect that an *outward* relaxation (or expansion) of the same magnitude would occur on electron capture. The sign of this relaxation is consistent with and can be rationalized in terms of the physical model for the O-V pair, as will be discussed in the next section.

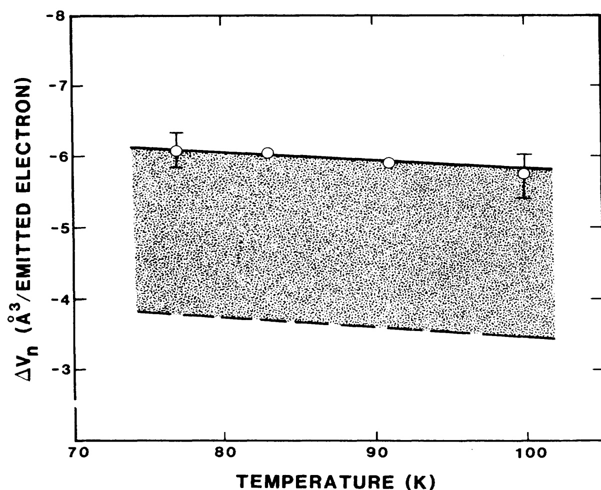

FIG. 7. Temperature dependence of the lattice volume relaxation accompanying electron emission from the O-V pair deep level in silicon.

The magnitude of the volume relaxation in Fig. 7 appears quite large, but it is necessary to put it into the proper perspective. To do so we note the following. At 100 K the average of the two bounds in Fig. 7 is $\Delta V_n = -4.6$ Å^3 per emitted electron. In Si the near-neighbor Si—Si bond length, r, is 2.35 Å, which we take to be also about the average distance between the O-V pair defect and its four nearest Si neighbors (see Sec. IV E). A sphere of radius 2.35 Å around the defect has a volume $V_0 = 54.3$ Å^3. If to a first approximation all of the relaxation is taken up by the nearest-neighbor shell of Si atoms, then $\Delta V_n / V_0$ at 100 K is -8.47%. This corresponds to a $\Delta r / r_0$ of -2.8% or a decrease in r of 0.07 Å. This means that upon electron emission the near-neighbor Si atoms relax *inward* by 0.07 Å, which is relatively large.

Our assumption that all of the relaxation is taken up by the first shell of Si atoms cannot be strictly correct. Recent experimental results on the lattice relaxation associated with arsenic (As) impurities in Si show that the relaxation of the first shell of Si atoms around the As is about 10 times larger than that of the second shell.[17] On the basis of these results we suspect that the above assumptions may lead to an about 30% overestimate in the magnitude of Δr. This would reduce the Δr from 0.07 to 0.05 Å.

The value of ΔV_n for the O-V acceptor level is twice as large as that for the deep gold acceptor level in Si.[4,9] The larger value for the O-V acceptor is qualitatively consistent with intuitive expectation. The Au atom is much larger than Si and there is simply less room for volume relaxation in its vicinity. The oxygen atom, on the other hand, is smaller than Si, and the nature of the O-V pair (discussed below, Fig. 8) is conducive for larger

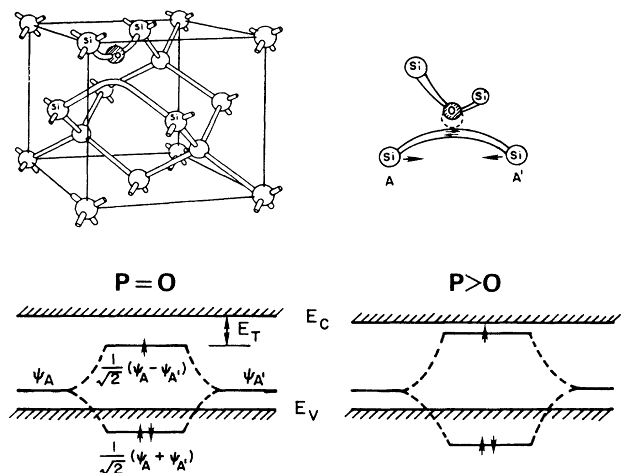

FIG. 8. Model of the O-V pair defect deduced from the studies of Refs. 1 and 2 (see text for details). The lower portion of the figure depicts the pressure (P)-induced increase in the splitting between the bonding $[(1/\sqrt{2})(\psi_A + \psi'_A)]$ and antibonding $[(1/\sqrt{2})(\psi_A - \psi'_A)]$ states of the Si—Si molecular bond.

relaxation.

The results in Fig. 7 suggest a small decrease in the magnitude of ΔV_n with increasing temperature. Reference to Eqs. (4), (5), and (7) and the results of the preceding section shows that this effect is related to the increase in the magnitude of the pressure dependence of the entropy with increasing T.

E. Model for the O-V pair defect

We now wish to discuss several features of our pressure results in terms of the generally accepted model for the O-V pair defect. This model is based on EPR and ir data and leads to the conclusion that this center consists of a single oxygen atom in a lattice vacancy formed when a mobile vacancy is trapped by an interstitial oxygen atom.[1,2] According to Watkins and Corbett,[2] one can picture the formation of this center as depicted schematically in Fig. 8. The Si vacancy is initially surrounded by four dangling bonds, one from each of its Si neighbors. The oxygen bridges two of these bonds forming an Si-O-Si "molecule." The remaining two silicons pull together forming a Si—Si molecular bond.

To form this Si—Si bond, the broken bond orbitals on the two Si atoms (represented in Fig. 8 by the wave functions ψ_A and ψ'_A) must overlap, and this overlap splits the resulting molecular orbitals into bonding $(\psi_A + \psi'_A)$ and antibonding $(\psi_A - \psi'_A)$ orbitals.[2] In the neutral state configuration the two electrons (one from each Si) are paired off in the bonding orbital, and the center is not paramagnetic. The bonding orbital falls probably outside the band gap (i.e., below E_v), whereas the antibonding orbital is in the gap as depicted in Fig. 8. Upon electron capture, the trapped electron goes into the antibonding orbital[2] whose energy corresponds to the trap energy E_T at $E_c - 0.164$ eV. In this negatively charged state the center is paramagnetic.

With the application of pressure the overlap between the Si orbitals forming the Si—Si molecular bond increases and this should result in increased splitting between the bonding and antibonding molecular orbitals. Consequently, the level E_T can be expected to move higher in the gap as depicted in Fig. 8. This is what we observe (see Fig. 5). it is interesting to note that this result appears to be a general result for vacancylike centers in Si. Recent pressure results on the gold[9] and platinum[18] acceptor levels, which are believed to have vacancylike character,[19,20] yield a qualitatively similar result.

In forming the Si—Si bond in the neutral state the two Si atoms pull together[2] as depicted in Fig. 8, and this should result in considerable strain and, therefore, *inward* relaxation in the surrounding lattice. On capturing an electron into the antibonding state, however, the Si atoms relax back towards their normal lattice positions, lowering the strain energy.[2] This picture is fully confirmed by our results which show inward relaxation on electron emission, and thereby the necessarily outward relaxation on electron capture. Thus, our results support the model and provide the first and (as far as we know) the only quantitative measure of this relaxation.

V. CONCLUDING REMARKS

The results of this paper have illustrated several aspects of the usefulness of hydrostatic pressure as a variable in studying the properties of deep electronic levels. The paper has dealt specifically with the O-V acceptor, but the approach is applicable to semiconductors in general. It is hoped that similar studies on several semiconductors will reveal features and trends which will improve our understanding of the physics of deep levels. In this regard, there are very close qualitative similarities between the present pressure results on the O-V acceptor and those reported on the gold (Au^0) acceptor[9] and platinum (Pt^-) acceptor[18] in n-type Si. This similarity in pressure response emphasizes some similarities in the basic nature of the three centers. More specifically, the pressure results are consistent with Watkins's recently proposed vacancylike model[19] for these three defects. This model is based in part on the similarity of the EPR spectra of these defects to the spectrum of the negatively-charged silicon vacancy, V^-. This similarity and the arguments presented earlier in the paper suggest that the Si vacancy, V^-, should exhibit a large volume relaxation ΔV_n, which is comparable in magnitude to, or perhaps even larger than, that for the O-V acceptor. In all of these cases, the captured electron goes into an antibonding orbital, and consequently the relaxation is outward (inward) on electron capture (emission) and the levels move higher in the gap with pressure.

The quantitative determination of the lattice volume relaxation accompanying electron emission and capture from analysis of the pressure results is, as far as we know, the only known experimental means for obtaining this relaxation. Knowledge of this relaxation is important to the development of accurate deep-level potentials and to the understanding of many deep-level phenomena in semiconductors such as extrinsic self-trapping and recombination-enhanced defect reactions.

Extended x-ray absorption fine-structure (EXAFS) measurements are beginning to be applied to the measurements of lattice relaxations associated with the presence impurities.[17,21] They have not been applied to the study of relaxations associated with carrier emission and capture processes. One very serious limitation of the method is that it requires very high impurity (or defect) concentrations ($>10^{19}$ cm^{-3}). Thus, it cannot be used in the great majority of cases of interest (such as the present case of the O-V pair defect) where the defect concentration are typically orders of magnitude smaller.

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