Pressure dependence of impurity levels in semiconductors: The deep gold acceptor level and shallow donor and acceptor levels in silicon

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The effects of hydrostatic pressure on the properties of the deep gold (Au) acceptor level and on the binding energies of shallow donors and acceptors in silicon are presented and discussed. The pressure dependences of the Gibbs free energy, enthalpy, and entropy associated with electron emission from the Au acceptor were determined from measurements of the electron emission rate and electron-capture cross section (σ_n) as functions of pressure and temperature. The results allow determination of the breathing-mode lattice relaxation accompanying electron emission from this center. The relaxation is found to be relatively large and inward (i.e., contraction). This appears to be the first quantitative determination of this relaxation for any electronic level in any semiconductor. Other highlights of the results on the Au acceptor are the findings that (i) the energy of this level is pinned to neither the conduction- nor valence-band edges, contrary to earlier belief and (ii) σ_n, which is known to be temperature independent, is also pressure independent. This latter result is discussed in terms of possible mechanisms for nonradiative electron capture. For the shallow donors and acceptors, the pressure derivatives of the binding energies are over an order of magnitude smaller than those of the energy gap and the Au acceptor, i.e., these levels remain essentially pinned to their corresponding band edges, as expected. These results can be understood in terms of effective-mass theory.

I. INTRODUCTION

Although pressure studies of the bulk properties of semiconductors are extensive and have contributed substantially to our understanding of the electronic structure of this class of materials,[1] relatively little pressure work has been done on impurity and defect states. Shallow, or hydrogenic, levels are generally well understood and their properties are satisfactorily described within the framework of effective-mass theory. The current understanding of deep levels, on the other hand, is rather limited.

We have been investigating the effects of hydrostatic pressure on impurity and defect levels in a variety of semiconductors. Several factors motivate our work.

(i) The poor state of understanding of deep levels and the hope that pressure results will lead to a better understanding of the physics of such levels. Here pressure results may make it possible to test proposed models, and, in conjunction with theory, may allow identification of the microscopic defects responsible for these levels.[2] This is in part due to the influence of pressure on defect potentials. Knowledge of these potentials is crucial to the understanding of deep levels. Additionally, pressure results contain, in principle, information on the lattice relaxation associated with the formation of defects, as well as with the emission and capture of carriers at deep levels.[3] Relatively large relaxations can be expected at deep levels because the localized nature of their potentials leads to strong electron-lattice coupling.

(ii) Comparisons of the pressure dependences of deep and shallow levels can provide new physical insight. The large ionization energies of deep levels arise because of strong potentials which act to localize the electronic wave functions near the sites of impurities or defects. Such potentials are dominated by short-range forces which are strong functions of the interatomic separation (or pressure). By contrast, shallow levels are dominated by long-range forces (or Coulomb potentials) which are much less sensitive to interatomic separation. Thus, the two types of levels can be expected to have widely different pressure responses. In fact, the magnitude of the pressure dependence of the binding energy of a level is an excellent means of distinguishing between shallow and deep levels.[4,5] This is particularly useful in borderline cases and in cases where this distinction cannot be made simply on the basis of the location of the level in the gap. Several examples can be cited to illustrate the latter point. The In acceptor in Si is located 160 meV above the valence band but behaves as a shallow level.[6] By contrast, the N level in GaP behaves as a deep trap despite the fact that its activation energy is only 10 meV.[5] Additionally, the thermal donor levels in Si (located at 60, 120, and 200 meV below the conduction band E_c) behave like shallow levels, whereas the A center (an oxygen-vacancy pair acceptor level located 160 meV below E_c) is a deep level.[7]

(iii) Pressure studies provide a better understanding of the temperature dependences of the properties of defect states by making it possible to separate the temperature effects at constant pressure into their volume-dependent and volume-independent contributions.[8] The latter contributions arise because of anharmonic interactions.

In the present paper we report on the effects of pressure on the deep gold acceptor level as well as on shallow donor and acceptor levels in silicon (Si). The measurements were performed over a relatively broad temperature range. A brief account of some of our early results was

presented elsewhere.[4,9] Gold is a technologically important dopant in Si used to control carrier lifetime, and the Au acceptor has been one of the most widely investigated deep levels in semiconductors, but it is still not understood microscopically. As we shall see, the pressure results provide some new insights into the nature of this level and allow evaluation of the lattice volume relaxation associated with electron emission from it. As far as we know, this latter feature may represent the first quantitative evaluation of lattice relaxation accompanying carrier emission from any deep level. The experimental techniques used are summarized briefly in the following section, and this is followed by presentation and discussion of the results.

II. EXPERIMENTAL DETAILS

The deep Au acceptor level was studied by transient capacitance[10] and deep-level transient capacitance spectroscopy (DLTS) techniques,[11] 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 phosphorous doped at $\sim 4\times 10^{15}$ cm^{-3}, and the p region was boron-doped at 5×10^{18} cm^{-3}. The gold concentration was uniform at $\sim 1\times 10^{14}$ cm^{-3}. 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, 4, and 10 V and yielded the electron thermal emission rates, emission energy, and their pressure dependences. The effects of electric field on these properties were negligible over this range of bias voltages, and the emission rates and energies at atmospheric pressure were in good agreement with earlier work.[12]

We also measured the pressure dependence of the electron-capture cross section of the Au acceptor level. This was determined from the variation of either the initial capacitance amplitude after reverse bias or the amplitude of the DLTS peak as a function of the length of the trap-filling pulse.[10,11,13]

The ionization energies E_i and their pressure dependences for shallow donors and acceptors were determined from measurements of the imaginary part of the low-frequency dielectric response, ϵ'' (or dielectric loss, $\tan\delta$), of Schottky-barrier structures as a function of frequency and temperature. In the temperature range where the carriers become ionized, both the real and imaginary parts of the dielectric response exhibit strong relaxational-type dispersion. In particular, as a function of temperature $\tan\delta$ exhibits a sharp, frequency-dependent maximum at a temperature $T_{\max}$.[14] At a given pressure, E_i is determined from such maxima from the relationship

$$\omega=\omega_0\exp(-E_i/kT_{\max}) , \tag{1}$$

where ω is the angular frequency of the measuring ac field and ω_0 is a constant. As we shall see in the following section, the data yield accurate values of the E_i's.

These measurements were made on thin plates (~ 0.4 cm^2 in area by ~ 0.05 cm thick) of high-resistivity ($\rho > 10^2\ \Omega$ cm), lightly doped single-crystal Si samples. The n-type samples were arsenic (As) doped, whereas the p-type samples were boron (B) doped. Gold electrodes were vapor deposited on the large crystal faces. The measurements were made in the frequency range 10^2–10^6 Hz using a high-accuracy ($>0.1\%$) three-terminal capacitance bridge and shielded leads and sample holder.

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 4 and ~ 400 K at different rates or accurately controlled at a fixed T 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 and Cu-AuFe thermocouples.

III. RESULTS AND DISCUSSION

A. The deep gold acceptor

As already noted, this important center has been much studied, but its microscopic nature is still controversial. Suggestions have ranged from the center being due to a simple Au substitutional impurity, or to an interstitial Au–vacancy complex, or to a more complex "family of closely related defects."[15,16] Recent work has emphasized the vacancylike character of this center.[17,18] Attempts to determine the temperature dependence of the energy of this center have also led to controversy as to which band edge, if either, the level is pinned to.[12] Engstrom and Grimmeiss[19] analyzed optical data as well as the temperature dependence of the thermal capture and emission of *holes* at this level and concluded that the acceptor level is pinned to the conduction band edge as a function of temperature. Dudeck and Kassing,[20] on the basis of small signal impedance and I-V measurements, came to the same conclusion. On the other hand, Brotherton and Bicknell[21] analyzed the temperature dependences of the thermal capture and emission rates of *electrons* at this acceptor level and concluded that this level may be pinned to the valence band edge. Later Lang *et al.*[11] analyzed all of the then-available data and concluded that the gold acceptor level can be viewed as pinned either to the conduction band or to the valence band depending on the method of analysis and the initial assumptions made. More recently van Staa and Kassing[22] concluded on the basis of DLTS measurements that this level is "temperature-independently pinned to the conduction band," whereas Kalyanaraman and Kumar,[23] using current transient and DLTS techniques came to the opposite conclusion, i.e., the level is pinned to the valence band. As will be shown below, the present pressure results make possible a definitive conclusion on this issue.

1. Electron emission rate and energy

In the present work we investigated electron emission and capture by the Au 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,[12] e_n,

$$e_n = \sigma_n \langle v_n \rangle N_c \exp(-\Delta G_n / kT) , \quad (2)$$

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

$$G = H - TS , \quad (3)$$

where H is the enthalpy and S is the entropy, Eq. (2) can be rewritten as

$$e_n = \sigma_n \langle v_n \rangle N_c \exp(\Delta S_n / k) \exp(-\Delta H_n / kT) . \quad (4)$$

In Eq. (4), 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.[12]

In interpreting the temperature and pressure dependences of e_n, we note the following. For the Au acceptor in Si, σ_n is known to be temperature independent over the range $\sim$80—400 K (Refs. 12 and 21) and, as we shall see later, we find it to be pressure independent as well. The thermal velocity is given by $\langle v_n \rangle = (3kT/m_n^*)^{1/2}$, where m_n^* is the electron effective mass. As will be seen in Sec. III B, the pressure dependence of m_n^* in Si is very weak, and thus we take the pressure dependence of $\langle v_n \rangle$ to be negligible. The density of states is given by $N_c = 2(m_n^* kT/2\pi\hbar^2)^{3/2} M_c$, where M_c is the number of equivalent minima in the conduction band. Its pressure is thus also negligible and partially cancels that of $\langle v_n \rangle$. On the basis of these considerations we thus see that the slope of a $\ln(e_n T^{-2})$ 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 of ΔG_n since from Eq. (2) and the above considerations we have

$$(\partial \ln e_n / \partial P)_T = -(kT)^{-1} (\partial \Delta G_n / \partial P)_T . \quad (5)$$

Knowing the pressure dependences of ΔG_n and ΔH_n allows determination of the pressure dependence of ΔS_n since from Eq. (3) we see that

$$(\partial \Delta G_n / \partial P)_T = (\partial \Delta H_n / \partial P)_T - T(\partial \Delta S_n / \partial P)_T . \quad (6)$$

At this point we should point out another consideration necessary for the interpretation of experimental pressure data. For the Au acceptor, electron emission is measured from the acceptor level (or trap), E_T, to the conduction band edge, E_c, and the isothermal 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.[24(a)] In this regard, it is helpful to consider two limiting cases.

Case (i). 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.

Case (ii). 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, $(\partial \Delta G / \partial P)_{T,\text{gap}} = -1.5$ meV/kbar.[1] By intrinsic pressure dependences of ΔG_n and other thermodynamic properties we here mean 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 Au acceptor, case (i) 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 be between the two bounds.

We have determined the isothermal pressure depen-

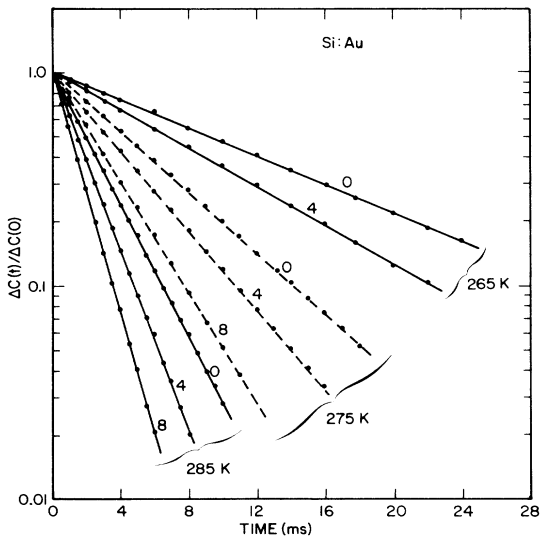

FIG. 1. Normalized capacitance transients for electron emission from the gold acceptor level in silicon measured at different pressures (indicated by the numbers 0, 4, and 8 in kbar) and temperatures. The slope of each line yields the emission rate which is seen to be strongly temperature and pressure dependent.

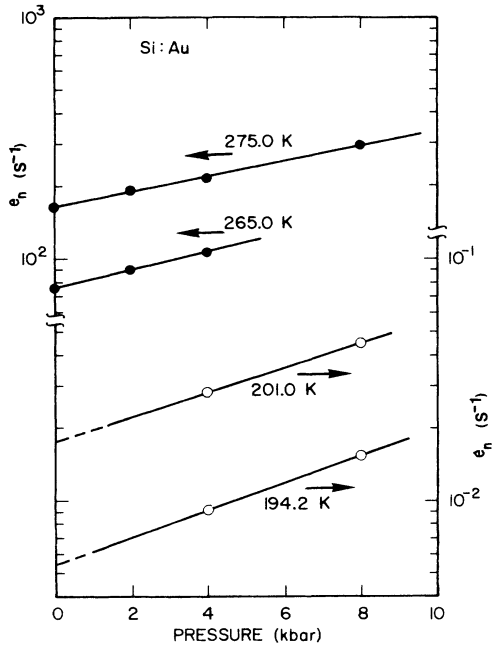

FIG. 2. The pressure dependence of the electron emission rate from the gold acceptor level in silicon measured at different temperatures. The open and solid symbols represent two different samples from the same batch.

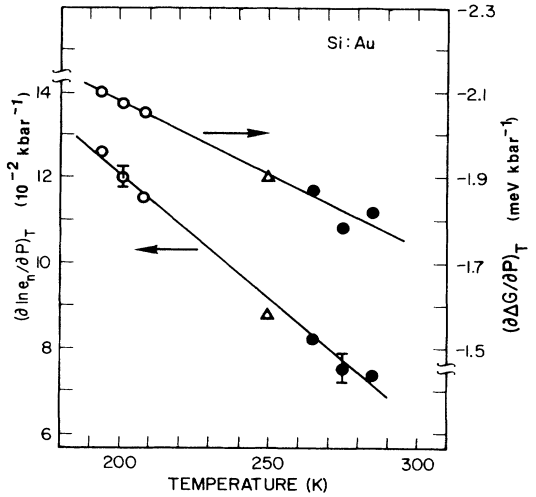

FIG. 3. Temperature dependences of the logarithmic pressure derivative of the emission rate and of the pressure derivative of the Gibbs free energy needed to emit an electron from the gold acceptor level in silicon. The open and solid circles represent data for two different samples and the open triangle is a datum point from Li *et al.* (Ref. 24).

dence of e_n from capacitance transients measured as a function of time after the application of reverse bias. Figure 1 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.

Figure 2 shows that e_n increases logarithmically with pressure, and that the slope $(\partial \ln e_n/\partial P)_T$, decreases markedly with increasing temperature. This temperature dependence is shown for all the present data in Fig. 3, where we also show the recent datum point of Li *et al.*[24] at 249.5 K. There is good agreement between this point and our results. Use of the slopes $(\partial \ln e_n/\partial P)_T$ in Eq. (5) yields the values of $(\partial \Delta G/\partial P)_T$ also shown in Fig. 3. This quantity decreases in magnitude from $\sim -2.1 \pm 0.2$ meV/kbar at 190 K to $\sim -1.75 \pm 0.2$ meV/kbar at 300 K. The range in these values represents the total experimental uncertainties.

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. The results are summarized in Fig. 4. At 1 bar the $e_n(T)$ data are in excellent agreement with earlier work[12] with $\Delta H_n = 0.553$ eV.

This enthalpy represents what the literature has identified as the ionization energy of the level, E_c-E_T. The increase in e_n with pressure results primarily from a decrease in ΔH or E_c-E_T, and this decrease is shown in the inset in Fig. 4. The decrease is linear with a slope of -2.6 ± 0.5 meV/kbar, implying that E_T *moves closer* to E_c at a rate of 2.6 meV/kbar.[25] For comparison we show by the dashed line in the inset in Fig. 4 the shift of the band-gap energy, E_g, with pressure, where the slope is -1.5 meV/kbar.[1] From the results in Fig. 4 we deduce that E_T *moves away* from the valence-band edge, E_v, at a rate of 1.1 meV/kbar.

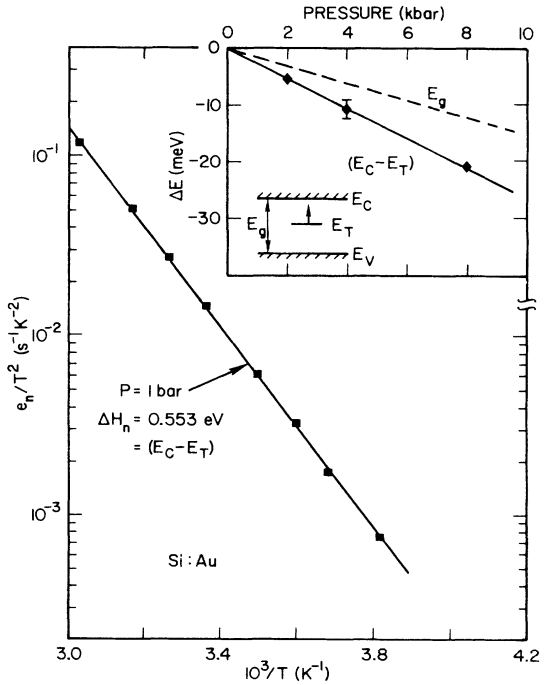

FIG. 4. Temperature dependence of the electron thermal emission rate from the gold acceptor level in silicon at 1 bar. The inset compares the pressure shift of the enthalpy ΔH (or $E_c - E_T$) with that of the band gap E_g, of silicon.

These results are important for they clearly show that, contrary to earlier belief,[12,19–23] the Au 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 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 and bands.

An earlier study of the pressure dependence of E_T of the Au acceptor level in Si exists.[26] The results were obtained indirectly from resistivity measurements as a function of pressure and are subject to considerable uncertainties in the data and in the approximations needed for their interpretation. It was found that, measured with respect to E_c, $dE_T/dp \cong -1.2$ meV/kbar at pressures up to 4 kbar and increases to -1.5 meV/kbar at ~ 25 kbar. Our slope is larger and is constant up to the 8-kbar limit of our experiments. We believe that the transient capacitance technique used in the present work is more direct and more accurate than the earlier method.

The fact that E_T moves away from E_v with pressure suggests that the acceptor level is determined by antibonding orbitals. This is consistent with the recent suggestion[17,18] that this level is vacancylike with its orbitals consisting mostly of dangling-bond states on the four Si nearest neighbors (see discussion below). Pressure forces the Si and Au atoms closer together, and this can be expected to force the antibonding states higher in the gap. This is what we observe.

2. *Electron capture cross section*

There are numerous measurements of the electron capture cross section, σ_n, of the gold acceptor level in Si. The data available up to around the year 1980 were reviewed by Lang *et al.*[12] Reported values of σ_n differ by as much as a factor of 30. Lang *et al.* analyzed the data and noted a correlation between the value of σ_n and the ratio of Au concentration, N_{Au}, to the shallow donor concentration, N_D. For samples with $N_{\mathrm{Au}}/N_D \lesssim 0.1$, σ_n values are in the range $(0.69-1.7)\times 10^{-16}$ cm^2. For our sample $N_{\mathrm{Au}}/N_D = 0.025$ and $\sigma_n = 1.2\times 10^{-16}$ cm^2. This value was obtained 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[13] that $\Delta C(0,\delta)$ is given by

$$\Delta C(0,\delta) \propto \Delta C(0,\delta\rightarrow\infty)[1-\exp(-n\sigma_n v_n \delta)] , \qquad (7)$$

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 ($\delta \geq 5$ μs in the present case). 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 $-n\langle v_n\rangle\sigma_n$.[27] Some data for one of the present samples are shown in Fig. 5.

Although there are quantitative differences in the reported values of σ_n, there is general agreement that σ_n is independent of temperature over the range 77–450 K.[12,21] We find that σ_n is also independent of pressure, within

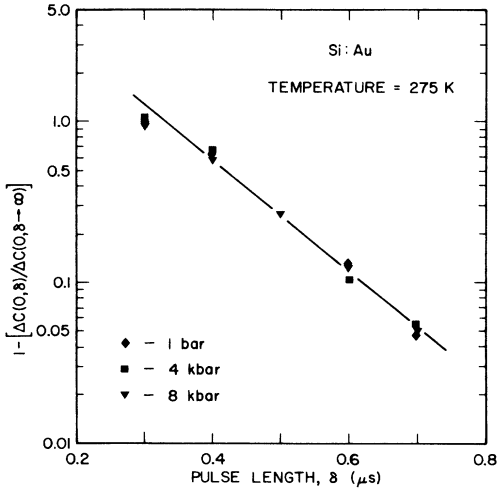

FIG. 5. Normalized initial capacitance amplitude after reverse bias as a function of filling pulse duration for the gold acceptor level in silicon measured at 275.0 K and different pressures.

experimental uncertainty, at least up to 8 kbar, as can be deduced from the results in Fig. 5. A similar result was recently found by Li *et al.*[24] in pressure measurements at 249.5 K. The temperature and pressure data are summarized in Fig. 6.

The lack of temperature and pressure dependences of σ_n raises some interesting questions about the mechanism responsible for nonradiative electron capture at this deep acceptor level. There appears to be no established mechanism at present, and we wish to examine the different possibilities in view of the temperature and pressure results.

Three mechanisms are generally invoked to explain nonradiative capture which involves large energy dissipation. These are capture by (1) an Auger process, (2) a cascade process, or (3) multiphonon emission (MPE).

In Auger capture the energy lost by the capture of a free carrier is taken up by the excitation of another nearby carrier. This process is highly probable in samples with

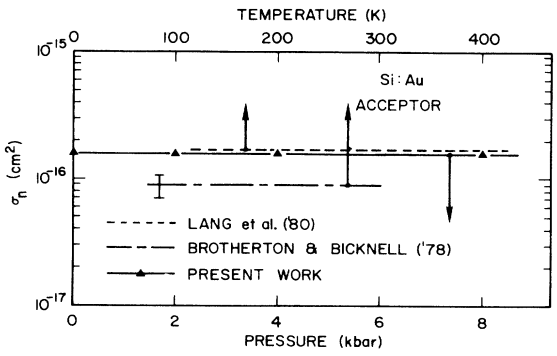

FIG. 6. Electron capture cross-section data for the gold acceptor level in n-silicon samples with $N_{\mathrm{Au}}/N_D \lesssim 0.1$ showing the remarkable lack of any temperature or pressure dependence.

large free-carrier concentration, and, for such free-carrier Auger capture, σ should be a strong increasing function of the carrier concentration. Such a process can be expected to exhibit very weak temperature or pressure dependence, and can thus conceivably be operable at the Au acceptor level. However, most of the samples of interest,[12] including our own, have carrier concentrations on the order of only 10^{15} cm^{-3}, and it is unlikely that free-carrier Auger capture is sufficiently probable at this concentration to yield $\sigma_n \sim 1\times 10^{-16}$ cm^2. Additionally, the data of Lang *et al.*[12] (their samples *A* and *B*) do not exhibit the dependence of σ_n on carrier concentration expected for this process. Specifically, the sample with the higher free-electron concentration gave the smaller σ_n. Thus, we must conclude that free-carrier Auger capture is not the likely mechanism.

In the cascade process, the carrier is captured into a highly excited state. It loses its energy by dropping down a series of closely spaced excited states, emitting one phonon after each step.[28] A long-range interaction between the charge carrier and the polarizability of the impurity center is believed to be capable of producing a ladder of excited states when the polarizability is large enough. However, for a very deep midgap level such as the Au acceptor, it is difficult to conceive of such a ladder of states spanning from the trap level to the band edges. Thus, it seems highly unlikely that cascade capture is applicable to the present case. Additionally, cascade capture leads to a temperature-dependent σ,[29] and this is not observed for the Au acceptor.

In the MPE process capture occurs by lattice-vibration-induced crossing of free, or weakly bound, electronic states with strongly bound electronic states.[30] There is strong coupling between the lattice and the deeply bound state, and the energy lost by the captured carrier generates lattice phonons. To be captured, the free carrier may have to overcome an energy barrier, E_B, and at sufficiently high—temperature semiclassical theory leads to the prediction that σ is thermally activated,[30] i.e.,

$$\sigma=\sigma_\infty \exp(-E_B/kT) . \tag{8}$$

In fact, a strong temperature dependence of σ is usually taken as evidence for carrier capture by MPE. In such a case E_B and the electron-phonon coupling can be expected to be fairly pressure sensitive, and, indeed, are found to be so.[31]

The absence of any temperature (up to $\sim$450 K) or pressure dependence of σ_n for the Au acceptor level may on first view be taken as evidence that MPE is not the mechanism for electron capture at this level. However, as emphasized by Ridley,[32] the conditions necessary for the high-temperature approximation represented by Eq. (8) to apply are rarely met in semiconductors. Ridley performed a quantum mechanical calculation of the multiphonon nonradiative transition rate without recourse to either the Condon or adiabatic approximations. By adopting a single-frequency model, he derived expressions for both the high- and low-temperature regimes. At high temperatures his result leads to an expression for σ of the same form as Eq. (8), however at low temperatures he finds that the capture rate W ($\equiv\sigma\langle v\rangle N$) is given by

$$W=\omega\frac{\pi}{(\hbar\omega)^2}\mathbf{V}\cdot\mathbf{V}\frac{S^{p-1}e^{-S^*}}{(p-1)!}R_0(\bar{n}+1)^p e^{-2\bar{n}S^*} , \tag{9}$$

where ω is the frequency of the equivalent mode, S^* is the Huang-Rhys factor, p is the number of phonons involved in the capture process, $\bar{n}\equiv[\exp(\hbar\omega/kT)-1]^{-1}$ is the phonon population factor, $\mathbf{V}\cdot\mathbf{V}$ is an electron transition matrix element, and R_0 is an interaction parameter which is rather insensitive to p and S^*. Although several of its parameters are temperature dependent, Eq. (9) can lead to a temperature-independent σ depending on the choice of T and the various parameters.[32]

Morante *et al.*[33] have recently performed quantum calculations of the capture rate similar to Ridley's and obtained a low-temperature expression which they applied to the Au acceptor level in Si. As the Debye temperature of Si is $\sim$625 K, the low-temperature limit is the appropriate one to describe $\sigma(T)$ data up to $\sim$450 K. Morante *et al.*'s result satisfactorily explains the weak temperature dependence of W_n (or temperature independence of σ_n) observed experimentally. Interestingly, they find that W_n (or σ_n) depends very sensitively on the value of S^*, and they suggest that the large differences in the reported values of σ_n can be explained on the basis of different S^* values for the different samples. They further suggest that S^* can be strongly influenced by internal stress produced by growth and diffusion processes.

In terms of Ridley's[32] and Morante *et al.*'s results, the absence of a measurable pressure dependence of σ_n must mean that either the effect is too small to determine within the experimental uncertainty, or there are canceling pressure effects among the various parameters involved. We suspect that it is the latter. Since several parameters with unknown pressure dependences are involved, it is difficult to be more specific.

It thus appears that the MPE process is capable of explaining free-electron capture, by the Au acceptor in *n*-type Si. As a large energy is dissipated by this capture and σ_n is also relatively large, considerable lattice relaxation must accompany the capture process. As we shall see below, this is indeed the case.

3. *The entropy factor*

As is known[12] and can be easily confirmed from the above data and Eq. (4), the Au acceptor has a large total entropy change, ΔS_n, accompanying electron emission. Thus, e.g., at $T=250$ K and for samples with $N_{Au}/N_D \lesssim 0.2$ (as in the present case) ΔS_n falls in the range[12] 3.0 K—3.9 K. This ΔS_n is the sum of changes in entropy due to electronic degeneracy and due to atomic vibrational changes.

Going back to Eq. (6), the pressure dependences of ΔG and ΔH allow a determination of the 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 $\sim -2.6\times 10^{-3}$ meV/kbar K at $\sim$190 K to $\sim -2.9\times 10^{-3}$meV/kbar K at $\sim$300 K. In considering these numbers, we should emphasize that the quantity $T(\partial\Delta S/\partial P)_T$ in Eq. (6) is determined by the difference

between two numbers which are close in magnitude, namely the pressure derivatives of ΔG and ΔH. Thus, the absolute magnitude of $(\partial\Delta S/\partial P)_T$ involves 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, should be valid.

Since the intrinsic ΔS_n for the Au acceptor $(3.0k-3.9k)$ is larger than the ΔS associated with excitation across the gap ($\sim 2.7k$ at 250 K),[34(a)] and because of the deformed nature of the lattice around the Au impurity, we presume that the above pressure dependence of ΔS reflects, at least qualitatively, the intrinsic effect associated with the emission process, 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 become smaller as the lattice becomes stiffer with compression. A large vibrational entropy is also consistent with a relatively large lattice relaxation (see following 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 understood by a similar argument, namely, that increasing T softens the lattice and thereby makes the effect of compression more pronounced.

4. *Lattice relaxation associated with electron emission*

As already noted (Sec. III A 1), the pressure dependence of e_n provides a direct measure of $(\partial\Delta G/\partial P)_T$ which is the total effect consisting of the intrinsic pressure derivative $(\partial\Delta G_n\partial P)_T$ plus a contribution from the shift of the gap. Now from the well-known thermodynamic relation

$$dG = VdP - SdT\ , \tag{10}$$

it is readily seen that

$$(\partial\Delta G_n/\partial P)_T = \Delta V_n\ , \tag{11}$$

i.e., the isothermal pressure dependence of ΔG_n measures a volume change, which we represent by ΔV_n. What is the physical significance of this thermodynamic volume change? We have conjectured that it is the volume change, or breathing mode lattice relaxation of the defect which accompanies electron emission.[3] The present results thus provide a direct measure of this relaxation at the Au acceptor level. This was discussed in Ref. 3, but the values of ΔV_n presented there represent the upper bound on ΔV_n. This is case (i) discussed in Sec. III A 1. The lower bound, i.e., case (ii), is obtained by subtracting from the $(\partial\Delta G/\partial P)_T$ results in Fig. 3 the shift of the gap (-1.5 meV/kbar). The overall results are shown in Fig. 7.

We note from Fig. 7 that ΔV_n is negative, implying that the lattice relaxes inward (i.e., contracts) upon electron emission from the Au acceptor. We expect that an outward relaxation (or expansion) of the same magnitude would obtain upon electron capture. The sign of this relaxation has been rationalized[3] in terms of a model[17,18]

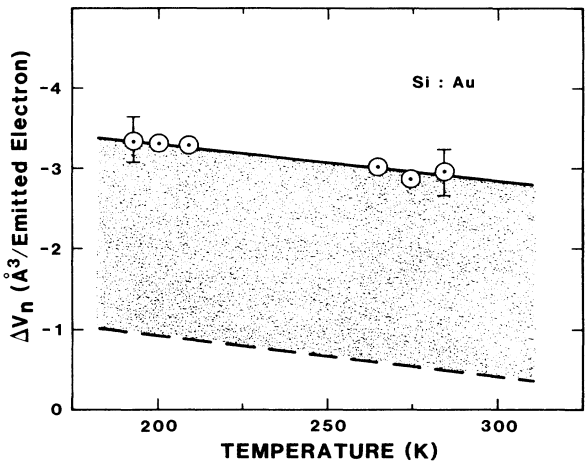

FIG. 7. Temperature dependence of the lattice volume (breathing-mode) relaxation, ΔV_n, accompanying electron emission from the Au acceptor level. The data points represent the upper bound and the dashed line in the lower bound on the magnitude of ΔV_n as discussed in the text.

which treats the Au center basically as a perturbed vacancy whose electronic structure is that of a closed $5d^{10}$ shell (from the Au) inside of a vacancy, i.e., $5d^{10}+V^-$.

To put the magnitude of the volume relaxation in Fig. 7 in the proper perspective, we note the following. At 250 K the average of the two bounds in Fig. 7 is $\Delta V_n = -1.9$ Å^3 /emitted electron. The near neighbor Si—Si bond length, r_0, in Si is 2.35 Å which we also take to be the average distance between the Au center and its four nearest Si neighbors. A sphere of radius $r_0 = 2.35$ Å around the Au center has a volume $V_0 = 54.3$ Å.^{3} Thus $\Delta V_n/V_0$ at 250 K is -3.5%. This corresponds to $\Delta r/r_0 = -1.2\%$ or a decrease in r_0 of 0.028 Å. This means that upon electron emission the nearest-neighbor Si atoms around the defect relax *inward* by ~ 0.03 Å. Here we have assumed that all of the relaxation is taken up by the first shell of Si atoms around the Au, which should be a good first-order approximation.

The results in Fig. 7 suggest a small decrease in the magnitude of ΔV_n with increasing T. Reference to Eqs. (5), (6), and (11) and our earlier discussion shows that this effect is related to the increase in the magnitude of the pressure dependence of the entropy with increasing T. Despite the spread in the magnitude of ΔV_n, its suggested temperature dependence appears to be larger than what can be expected on the basis of normal lattice considerations. This is most likely a manifestation of the fact that the highly localized and perturbed nature of the defect center is far different from a normal lattice site.

5. *Models for the Au acceptor*

As already noted, there has been much controversy about the microscopic nature of the Au acceptor in Si. Discrepancies in the reported values of the energy and capture cross section of this level have been taken as evidence that there is not a single well-defined Au defect, but rather a family of Au-related defects.[12] Also controversial has been the question of whether or not the Au donor

and acceptor levels are related to the same or different defects.[12,34(b)] Despite these controversies, it seems almost certain that the acceptor is vacancy related. There have been long-standing suggestions that this level is associated with vacancy complexes[35] or a Au interstitial-Si vacancy complex,[15] but the recent suggestion[17,18] that it is vacancylike probably comes closest to its real identity. As already discussed above, some aspects of the pressure results are consistent with this identification.

Another aspect of pressure results is their use along with uniaxial stress results for saying something about the local symmetry of the defect. Recently, Li *et al.*[24] gave a criterion for doing so. They specifically considered a defect level with a defect potential of T_d symmetry and concluded that for such a level the uniaxial stress coefficient of the energy of the level is isotropic and equal to $\frac{1}{3}$ the corresponding pressure coefficient. Since this equality is not at all obeyed for the Au acceptor,[36] Li *et al.* concluded that the defect potential was far from T_d symmetry, and, therefore, that the level is unlikely to have originated from a simple Au substitutional or interstitial. While the conclusion about the site symmetry not being T_d appears correct, we point out that the results do not necessarily rule out the Au being a substitutional impurity. As already noted, a substitutional Au atom leads most likely to an acceptor with configuration $5d^{10}+V^{-}$. For this configuration the site symmetry is dihedral D_{2d} (which distorts to C_{2v} by the Jahn-Teller effect) and not T_d.[17]

B. Shallow levels

Typical results of the dielectric loss (tanδ) versus temperature measured at different frequencies at 1 bar are shown in Fig. 8 for the As-doped sample. The curves exhibit well-defined maxima. An Arrhenius plot of the log of the frequency versus the reciprocal of the temperature corresponding to the maximum in tanδ, $T_{\max}$, yields an

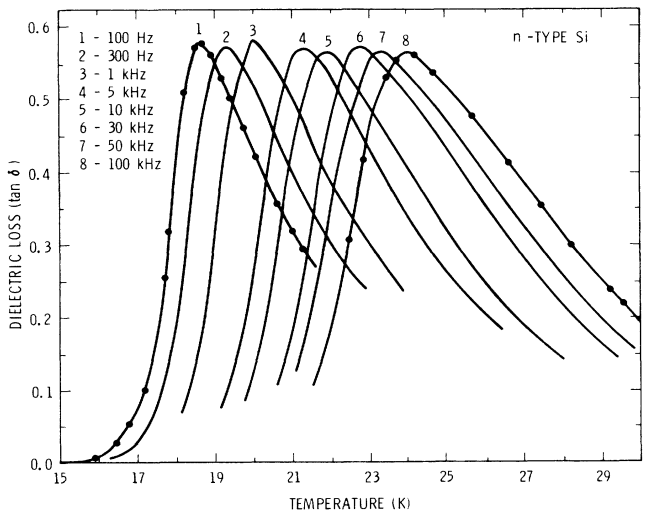

FIG. 8. Temperature dependence of the dielectric loss of an As-doped Si sample measured at different frequencies at 1 bar.

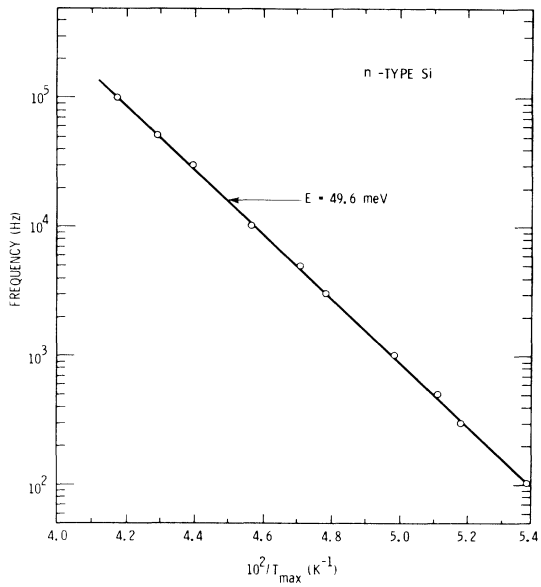

FIG. 9. Arrhenius plot of log frequency vs $1/T_{\max}$ according to Eq. (1) in the text for the As-doped Si sample in Fig. 8. The slope yields the ionization energy of the As doner.

ionization energy (E_i) for the As donor of 49.6±1.0 MeV (Fig. 9). This compares favorably with the accepted value of 49 meV.[37]

These measurements were repeated at different hydrostatic pressures up to 10 kbar. The results are qualitatively indistinguishable from those shown; the only difference being a small decrease in E_i. For n-type Si the decrease is $-(0.1\pm0.05)$ meV/kbar, which is just about the resolution of the measurement; but, we can definitely state that E_i decreases with pressure, i.e., the donor level moves slightly closer to the conduction band. For the B-doped p-type sample the pressure-induced shift in E_i is also small but positive, i.e., E_i moves slightly away from the valence band. The results are summarized and compared with earlier results as well as with the pressure-induced shift of the indirect gap in Table I.

Earlier, Holland and Paul[6] determined the pressure dependences of the ionization energies of As donors and In and Al acceptors in Si from the changes in the resistivity with pressure measured at 50 K for Si samples doped with these impurities. Their results are given in Table I. Analysis of the resistivity data to yield dE_i/dP is indirect, requiring knowledge of the pressure dependences of the mobilities (including both lattice and impurity scattering) and the effective masses. As these dependences are not very well known and the pressure derivatives dE_i/dP are small, the analysis of the resistivity data involves considerable uncertainties, as the authors indicate. Despite this concern, our values of dE_i/dP for both n- and p-type samples agree in sign with the values of Holland and Paul. Given the small absolute values of these pressure derivatives and the fact that they are close to the limit of detectability, we regard the numerical agreement between the two sets of results as satisfactory.

TABLE I. Pressure dependence of various energy levels in silicon.

Type of level	E (meV)	dE/dP (meV/kbar)	Reference
Donor (As): $E_c - E_D$	49.6	-0.1 ± 0.05	Present work
Donor (As)	49	-0.05	Reference 6
Acceptor (B): $E_A - E_v$	47	$+0.1 \pm 0.1$	Present work
Acceptor (Al)	57	$+0.01$	Reference 6
Acceptor (In)	160	$+0.05$	Reference 6
Indirect gap: $E_c - E_v$	1160	-1.5	Reference 6
Acceptor (Au): $E_c - E_T$	553	-2.6	Present work

The important feature of the results for our present purposes is that the pressure derivatives of E_i are of the order of 0.1 meV/kbar or less, which is over an order of magnitude smaller than the pressure derivatives of the gap energy and of the Au acceptor energy. Thus, these levels remain essentially pinned to the nearest band edges, as expected for shallow levels.

These shallow levels can be described by effective mass theory according to which the ionization energy is that of a hydrogenic ground state and is given by[1,6]

$$E = \frac{e^4 m^*}{2\epsilon^2 h^2} , \tag{12}$$

where e is the electronic charge, m^* is the density of states effective mass and ϵ is the dielectric constant. The pressure dependence of E_i can thus be understood in terms of the changes in m^* and ϵ according to

$$\left[\frac{d\ln E_i}{dP}\right] = \left[\frac{d\ln m^*}{dP}\right] - 2\left[\frac{d\ln\epsilon}{dP}\right] . \tag{13}$$

The pressure derivative of ϵ is known and that of E_i is given in Table I. Thus, we can evaluate the pressure dependence of m^*.

The situation is simplest for n-type Si where the constant energy surfaces are ellipsoids of revolution leading to one effective mass, m_n^*. For the As-doped sample our data in Table I yield $(d\ln E_i/dP) = -2\times10^{-3}$ kbar^{-1}. Substitution of this value along with the value[8] $(d\ln\epsilon/dP) = -0.6\times10^{-3}$ kbar into Eq. (13) yields $(d\ln m_n^*/dP) = -3.2\times10^{-3}$ kbar.$^{-1}$. Use of the value of Holland and Paul[6] of $(d\ln E_i/dP) = -1\times10^{-3}$kbar^{-1} yields $(d\ln m_n^*/dP) = -2.2\times10^{-3}$ kbar^{-1}. In either case, it is seen that the decrease of E_i with pressure for the As-doped sample is dominated by the pressure dependence (decrease) of m_n^*. The decrease in ϵ with pressure leads to an increase in E_i, but this effect is more than counterbalanced by the pressure dependence of m_n^*.

For p-type Si the situation is complicated by the complex nature of the valence band leading to the presence of both light and heavy holes. This makes the interpretation of the pressure dependence of E_i less certain. Casual use of Eq. (12) in this case suggests that m_p^* (whatever it means) *increases* slightly with pressure, in contrast with the behavior of m_n^*.

IV. CONCLUDING REMARKS

In this work we have presented and contrasted the effects of pressure on a deep and on shallow electronic levels in Si. The much larger pressure effects in the case of the deep level is a manifestation of the highly localized wave functions and short-range nature of the potential describing the deep center. The results have shed considerable new light on the nature of the levels investigated.

One of the main highlights of the work is the evaluation of the breathing-mode lattice relaxation accompanying electron emission (or capture) from the deep Au acceptor. The results establish the sign and bound the magnitude of this relaxation. There is a great deal of discussion in the current deep level literature about lattice relaxation accompanying carrier capture or emission from deep levels.[38] These relaxations are important for the understanding of both the nature of deep levels and many deep level phenomena, e.g., persistent photoconductivity, the negative U phenomenon, and recombination-enhanced defect reactions. As far as we know, there are no prior experimental measurements of this relaxation for any deep level in any semiconductor, and it has been only recently that theory has begun to address them in a meaningful way.[39] The method presented in this paper provides this quantitative measure and is, therefore, highly significant. It should be applicable to all deep levels for which the pressure dependence of ΔG_n (or ΔG_p) can be evaluated from Eq. (2) or a comparable expression.

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