Lattice Relaxation Accompanying Carrier Capture and Emission by Deep Electronic Levels in Semiconductors

G. A. Samara and C. E. Barnes[(a)]
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 11 July 1986)

It is proposed that measurements of the isothermal pressure dependences of emission rates and capture cross sections can provide a quantitative measure of the lattice volume relaxation accompanying carrier capture and emission processes by deep levels. The method is demonstrated for the gold acceptor and the oxygen-vacancy pair (*A* center) levels in silicon. The results represent what is believed to be the first quantitative determination of these relaxations for any deep levels in any semiconductor.

PACS numbers: 71.55.Fr

The understanding of deep electronic levels introduced by impurities and defects in semiconductors is one of the most important remaining problems in semiconductor science. Because deep centers are characterized by strongly localized, lattice-perturbing potentials, it is natural to expect that lattice relaxations would occur in the vicinity of such centers and that additional relaxations would accompany electron or hole capture and emission processes at these centers. The existence of these latter relaxations, which are believed to be relatively large in some cases, is much discussed and debated in the literature,[1,2] but apparently there are neither experimental measurements of them nor satisfactory theory to evaluate them. Knowledge of these relaxations is important to the understanding of many deep-level phenomena such as extrinsic self-trapping, the persistent photoconductivity (PPC) effect, the negative-*U* phenomenon, and electron-hole recombination phenomena.

The purpose of this Letter is to propose and demonstrate that certain pressure experiments can provide a quantitative measure of the lattice volume relaxation accompanying carrier capture or emission processes. In what follows we describe the proposed method and present results on two important deep centers in silicon, namely, the gold acceptor and the vacancy-oxygen pair (or *A*) center. Relatively large relaxations are found for both.

It is known[3] that in a rigorous thermodynamic sense the forbidden band gap of a semiconductor is properly defined as the standard chemical potential, μ, for electron-hole creation in the reaction $0 \rightarrow e^+ + e^-$, where e^+ and e^- denote a free hole and a free electron belonging to the thermal distribution at the valence-band edge and the conduction-band edge, respectively. In a similar way, the proper thermodynamic energy needed to emit an electron or a hole from a defect level is the chemical potential for that process.[3,4] As a chemical potential, this energy represents the total energy difference between the two different charge states (i.e., before and after emission) of the defect in their relaxed conditions with the electron (hole) in the conduction (valence) band. It is generally expressed in the following two ways[3-5]:

$$\mu \equiv \left.\frac{\partial U}{\partial N}\right|_{S,V} \equiv \left.\frac{\partial G}{\partial N}\right|_{T,P}, \tag{1}$$

where N is the number of carriers and U, G, S, V, T, and P denote, respectively, the total internal energy, Gibbs free energy, entropy, volume, temperature, and pressure of the sample. The first definition is relevant to optical transitions, while the second applies to thermally stimulated transitions.[3,4]

It is the second of these definitions which is relevant for our present purposes, and the important point (as will become clear shortly) is that the total emission energy of a deep level can be expressed in terms of a Gibbs free energy, G. This is the proper form of energy to use in a Boltzmann factor or Fermi function.[3-5] We recall here that G is given by the well-known thermodynamic relation $G = H - TS$, where the enthalpy H is $H = U + PV$.

With the above considerations, it can be shown[4,5] that the proper forms of the well-known detailed balance equations which relate thermal capture and emission rates are

$$e_{n,p} = \sigma_{n,p} \langle v_{n,p} \rangle N_{c,v} \exp(-\Delta G_{n,p}/kT), \tag{2}$$

for electron (n) and hole (p) emission. In Eq. (2), e is the thermal emission rate, σ is the capture cross section, $\langle v \rangle$ is the average thermal velocity of the carrier, $N_{c,v}$ is the effective density of states in the conduction (valence) band, and ΔG the change in free energy upon the emission of a charge carrier from the deep level. We note that this ΔG *is not* the activation energy determined from an Arrhenius plot. The activation energy is easily shown to be ΔH.[3-5]

Taking the logarithmic partial derivative of e_n in Eq. (2) with respect to pressure at constant temperature, we have

$$\left(\frac{\partial \ln e_n}{\partial P}\right)_T = \left(\frac{\partial \ln \sigma_n}{\partial P}\right)_T + \left(\frac{\partial \ln \langle v_n \rangle}{\partial P}\right)_T + \left(\frac{\partial \ln N_c}{\partial P}\right)_T - \frac{1}{kT}\left(\frac{\partial \Delta G_n}{\partial P}\right)_T, \tag{3}$$

with a similar expression for e_p. Now from the well-known thermodynamic relation $dG = V\,dP - S\,dT$, it is readily seen that $(\partial \Delta G_n/\partial P)_T = \Delta V_n$, 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 conjecture here that, since ΔG_n is the change in free energy upon emission, then ΔV_n must be the volume change, or lattice volume relaxation, of the defect center which accompanies electron emission.[6] It is thus seen from the above that knowledge of the pressure dependences of e_n, σ_n, $\langle v_n \rangle$, and N_c provides a direct quantitative measure of ΔV_n. All of these pressure dependences can, in principle, be accurately measured or estimated.

The pressure dependences of e_n and σ_n can be measured by means of transient capacitance and/or current spectroscopies. For a variety of deep levels, including the ones to be discussed below, $|\partial \ln e_n/\partial P|_T$ is found to be on the order of 10%/kbar or larger.[7,8] The pressure dependence of σ_n can vary from $\simeq 0$ to several percent per kilobar.[7-9] The thermal velocity is $\langle v_n \rangle = (3kT/m_n^*)^{1/2}$, where m_n^* is the electron effective mass, so that $(\partial \ln \langle v_n \rangle/\partial P)_T = -\frac{1}{2}(\partial \ln m_n^*/\partial P)$. The effective 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, so that $(\partial \ln N_c/\partial P)_T = \frac{3}{2}(\partial \ln m_n^*/\partial P)_T$. Thus, we see that the pressure dependences of $\langle v_n \rangle$ and N_c partially cancel each other and that the sum of their logarithmic pressure derivatives in Eq. (3) is simply equal to $(\partial \ln m_n^*/\partial P)_T$. The pressure dependence of m_n^* is known for Si and several other semiconductors, with $|\partial \ln m_n^*/\partial P|_T$ on the order of 0.1%/kbar,[8,10] which is negligible compared to the magnitude of $(\partial \ln e_n/\partial P)$. For the Au acceptor and the A-center levels we shall see that $(\partial \ln \sigma_n/\partial P)_T \approx 0$, and, therefore, for these two levels ΔV_n is, to a very good approximation, simply equal to $kT(\partial \ln e_n/\partial P)_T$.

To demonstrate the above method we have investigated two important deep levels in Si: the gold (Au) acceptor and the oxygen-vacancy pair (or A center). We measured the isothermal pressure dependences of e_n and σ_n at different temperatures for both levels. Analysis of the results yielded the corresponding ΔV_n's and their temperature dependences.

The pressure dependences of e_n and σ_n were studied by deep-level transient-capacitance spectroscopy,[11] the measurements being done in the high-field depletion region of reverse-biased p^+-n junction diodes. The measurements were performed mostly at reverse biases of 2 and 4 V where the effects of electric field on e_n and σ_n were negligible. The diodes for both centers were fabricated from Czochralski-grown Si which was ion implanted and annealed. The n region of the diodes was P doped at 4×10^{15} cm^{-3} and the p region was B doped at 5×10^{18} cm^{-3}. The Au concentration was uniform at $\sim 1 \times 10^{14}$ cm^{-3}. The A center was introduced by gamma irradiation to a total dose of 5×10^8 rads. A 10-kbar apparatus mounted inside a low-temperature Dewar was used. Helium gas was the pressure medium. The temperature could be controlled to better than 0.1 K, and the pressure was measured to better than ±1% by use of a calibrated Manganin gauge.

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

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

where n is the free-carrier density and $\Delta C(0,\delta \to \infty)$ is the free-carrier density and $\Delta C(0,\delta \to \infty)$ is the saturated capacitance amplitude obtained at sufficiently long pulse duration. It is thus seen that a plot of $\ln\{1 - [\Delta C(0,\delta)/\Delta C(0,\delta \to \infty)]\}$ versus δ should yield, over a certain range of δ, a straight line whose

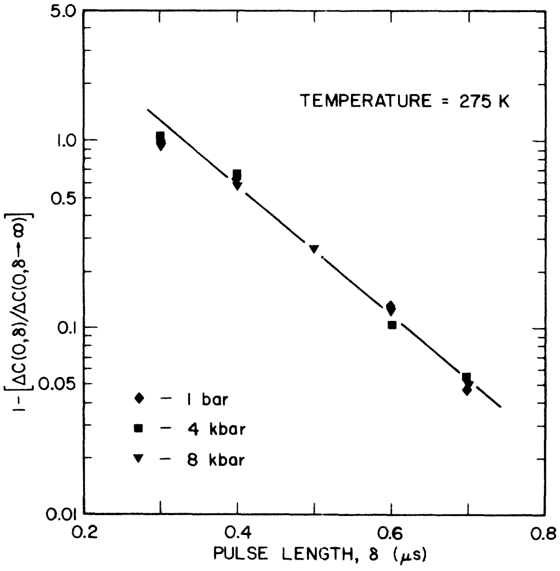

FIG. 1. Normalized initial capacitance amplitude after reverse bias as a function of filling-pulse duration for the gold acceptor.

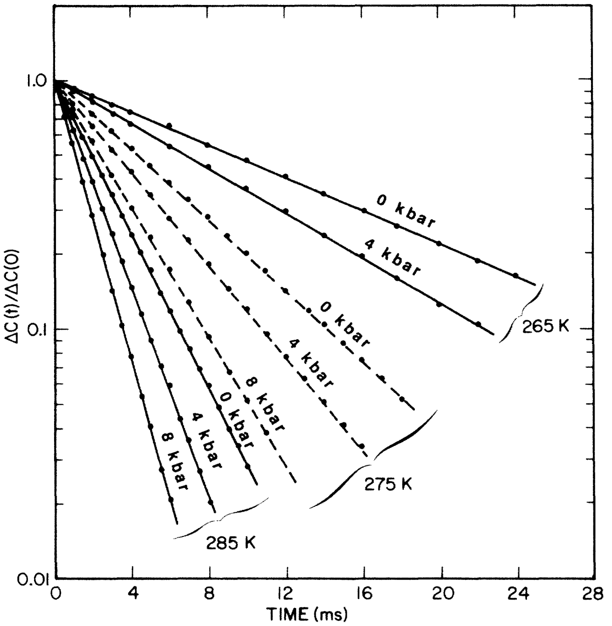

FIG. 2. Normalized capacitance transients for electron emission from the gold-acceptor level.

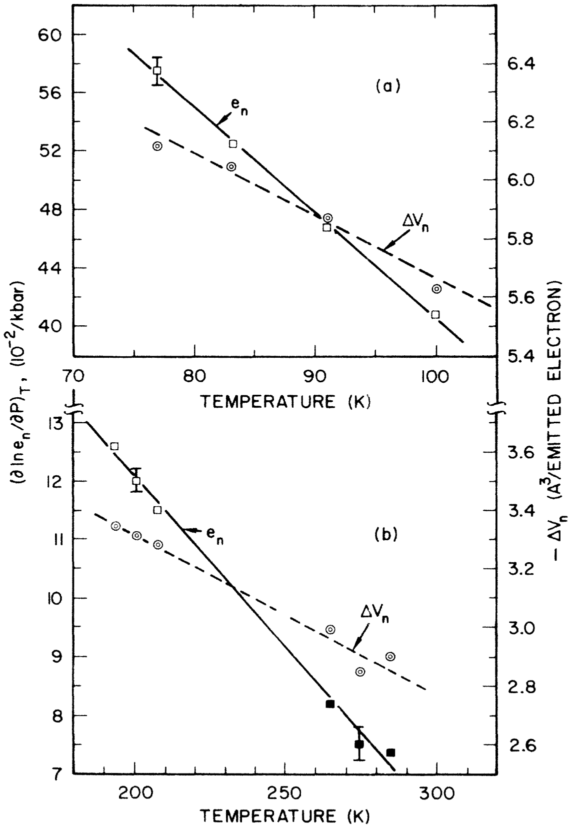

FIG. 3. Temperature dependences of the logarithmic pressure derivative of the electron-emission rate, e_n, and of the lattice volume relaxation which accompanies electron emission, ΔV_n, for (a) the deep *A* center and (b) the gold acceptor in Si.

slope equals $-n\langle v_n\rangle\sigma_n$. Some data for the Au-acceptor level at 275 K are shown in Fig. 1. Qualitatively similar data are obtained for the *A* center. We note that, within experimental uncertainty, the slope in Fig. 1 is independent of pressure at least up to 8 kbar. Since the pressure dependences of n and $\langle v_n\rangle$ are very weak, as discussed above, the results in Fig. 1 and similar results for the *A* center show that σ_n is independent of pressure, i.e., $(\partial \ln\sigma_n/\partial P)_T \approx 0$, for both of these centers. We emphasize that whereas σ_n is independent of pressure for the present two centers, this is not always the case.[9]

The isothermal pressure dependence of e_n was determined 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 for the Au-acceptor level displayed on a semilogarithmic plot. The slope of each straight line in the figure yields e_n at the indicated temperature and pressure conditions. Qualitatively similar results are obtained for the *A* center.

From data such as shown in Fig. 2 we find that e_n increases logarithmically with pressure,[8] and that the slope , $(\partial \ln e_n/\partial P)_T$, decreases markedly with increasing temperature. This temperature dependence is shown for the two levels in Fig. 3.

Use of the pressure derivatives of $\ln e_n$ in Fig. 3 yields the values of ΔV_n also shown in Fig. 3. These ΔV_n's are expressed in cubic angstroms per emitted electron. We note that ΔV_n is *negative* for both centers, which implies that the lattice relaxes *inward* (i.e., contracts) upon electron emission from these levels. We expect that an *outward* relaxation (i.e., expansion) of comparable magnitude would occur on electron capture.

The sign of the deduced relaxation for the two centers can be rationalized in the following way. It has been recently argued[12,13] that Au in Si behaves basically as a perturbed vacancy whose electronic structure is that of a closed $5d^{10}$ shell inside a vacancy, i.e., $5d^{10}+V^-$. The filled Au-derived atomic $5d$ level is localized below the valence-band edge, and the in-gap acceptor level (of t_2 symmetry) is vacancylike with its orbitals consisting most of dangling-bond states on the four Si neighbors. As this center is effectively negatively charged as a result of the $6s^{-1}$ electron from the Au and the Si dangling bonds, the capture of an electron by it can be expected to lead to a repulsive Coulombic interaction and an *outward* relaxation of the lattice, as concluded above. Upon subsequent emission of this electron, the lattice should then relax *inward,* as we find.

The accepted model for the A center, deduced from EPR results,[14] pictures this center as consisting of a single oxygen atom in a lattice vacancy. The oxygen bridges two of the four Si atoms around the vacancy, forming a Si-O-Si molecule, and the remaining two Si's pull together to form a Si-Si molecular bond. This latter process should produce an inward relaxation of the lattice. On capturing an electron (which goes into an antibonding orbital), the atoms relax back towards their normal lattice positions, lowering the strain energy.[14] This picture is fully consistent with our results, which show outward relaxation on electron capture and inward relaxation on emission.

To put the magnitudes of the above volume relaxations into better perspective, we note that the unit cell volume (V) of Si is 159 Å^3, so that $\Delta V_n/V \approx 2\%$ for the Au acceptor and 4% for the A center, both very large effects. Alternatively, the effective volume per Si atom is $V_{\rm Si} = 159/8$ or ~ 20 Å^3, so that $\Delta V_n/V_{\rm Si} = 15\%$ for the Au acceptor and 30% for the A center. The larger value of ΔV_n for the A center compared with the Au acceptor is consistent with intuitive expectation. The Au atom is much larger than Si and there is simply not much room for volume relaxation in its vicinity. The oxygen atom, on the other hand, is smaller than Si, and the nature of the A center (discussed above) is conducive to larger relaxation. The decrease in the magnitude of ΔV_n with increasing T is surprisingly large. This effect can be shown[8] to be due to the increase in the magnitude of the pressure dependence of the entropy with increasing T.

In summary, we have described a quantitative method for the evaluation of the lattice volume relaxation which accompanies charge-carrier emission (or capture) from deep electronic levels. The method was demonstrated for electron emission (capture), but similar considerations apply for holes. This evaluation of the relaxation is based on the use of the well-known detailed balance result [Eq. (2)] relating the thermal-emission rate to the change in the Gibbs free energy ($\Delta G_{n,p}$) which accompanies carrier emission from deep levels. The isothermal pressure dependence of ΔG yields a volume change (ΔV) which we conjectured is the lattice volume relaxation accompanying emission. The validity of this conjecture and evaluation rests on the validity of the use of ΔG as the proper thermodynamic form of the energy in the detailed balance equation. The present results are of central importance to the understanding of the many deep-level phenomena mentioned in the introduction. They could also prove to be crucial to the improvement of defect potentials and to the ultimate identification of the microscopic structure of many deep-level defects. It is hoped that the ideas presented here will stimulate further work on, and discussion of, the important issues involved in deep-level physics.

The technical assistance of L. V. Hansen is greatly appreciated. The work performed at Sandia National Laboratories was supported by the U.S. Department of Energy, under Contract No. DE-AC04-76DP00789.

---

[a] Present address: Aerospace Corporation, P.O. Box 92957, Los Angeles, CA 90009.

[1] See, e.g., *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986).

[2] D. V. Lang, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 489.

[3] H. Brooks, in *Advances in Electronics and Electron Physics,* edited by L. Marton (Academic, New York, 1955), Vol. 7, p. 85; C. D. Thurmond, J. Electrochem. Soc. **122**, 1133 (1975); J. A. van Vechten and C. D. Thurmond, Phys. Rev. B **14**, 3539 (1976).

[4] D. V. Lang, H. G. Grimmeiss, E. Meijer, and M. Jaros, Phys. Rev. B **22**, 3917 (1980).

[5] O. Engstrom and A. Alm, Solid State Electron. **21**, 1571 (1978).

[6] Similar thermodynamic considerations have been used for defect formation and ionic transport in solids [G. A. Samara, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1984), Vol. 38, p. 1, and references therein] and for the electron-hole creation process [R. W. Keyes, *ibid.,* Vol. 11, p. 149].

[7] A. Zylbersztejn, Appl. Phys. Lett. **33**, 200 (1978). See also K. Wünstel, O. Kumagai, P. Wagner, and W. Jantsch, Appl. Phys. A **27**, 251 (1982).

[8] G. A. Samara and C. E. Barnes, to be published.

[9] See, e.g., C. E. Barnes and G. A. Samara, Appl. Phys. Lett. **43**, 677 (1983).

[10] See, e.g., M. G. Holland and W. Paul, Phys. Rev. **128**, 30 (1962).

[11] C. T. Sah, L. Forbes, L. L. Rosier, and A. F. Tasch, Jr., Solid State Electron. **13**, 759 (1970); D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).

[12] G. D. Watkins, Physica (Amsterdam) **117&118B**, 9 (1983).

[13] J. L. A. Alves and J. R. Leite, Phys. Rev. B **30**, 7284 (1984).

[14] G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).