PHYSICAL REVIEW B VOLUME 25, NUMBER 8 15 APRIL 1982

Brief Reports

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Deep levels in semiconductors: A quantitative criterion

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(Received 31 December 1981)

The vague current classification of deep levels as not being shallow is replaced by a quantitative criterion. Deep levels, bound by the short-range impurity potential, exhibit pressure coefficients which are about 100 times larger than those of shallow states. Experimental results for chalcogen donors in Si are shown to agree with theoretical predictions.

Understanding and controlling deep levels in semiconductors is a major concern of semiconductor physics and device technology.[1,2] Traditionally, impurities with an activation energy larger than 0.1 eV are regarded as deep. The characteristic property of deep levels is the localization of the trap state due to the short-range impurity potential. This property is not necessarily reflected by the trap's binding energy. The *N* level in GaP, for example, exhibits properties typical for deep traps, although its activation energy[3] is only 10 meV.

This Report presents (i) a novel method to classify experimentally deep levels from shallow ones *independent* of their ionization energy, (ii) the first data under hydrostatic pressure of S,[4] Se, and Te in silicon constituting a stringent test of a recent model by Hjalmarson, Vogl *et al.*[5–7] (HVWD model), and (iii) a definitive threshold between shallow and deep states in two series of substitutional donors; Te is predicted and verified to represent the border between shallow and deep states.

The properties of sulfur, selenium, and tellurium impurities are best understood by assuming them to form double, substitutional donors (*D*) in Si (Refs. 8–10) and by assigning the *A* and *B* levels[8,9] of S, Se, and Te to the $D^+ \rightarrow D^{2+}$ and the $D^0 \rightarrow D^+$ transitions, respectively.[8] The pressure coefficients of the activation energy for these levels are determined here for the first time using a capacitance transient method.[11] Traps in the space-charge region of a *p-n* junction, which are initially filled with electrons, are emptied thermally after application of a reverse bias voltage. The corresponding change of the depletion-layer width man-

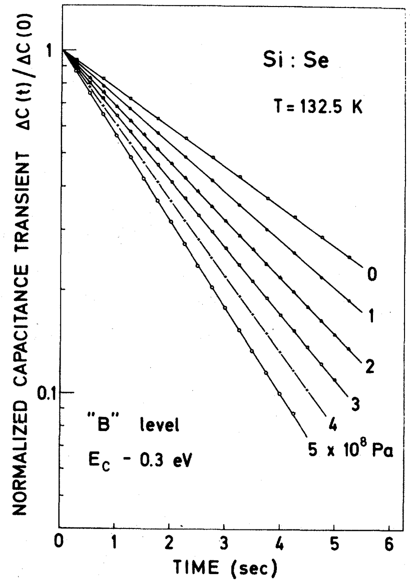

FIG. 1. Relative capacitance change of a p^+-n junction on Si:S due to the *B* level at 132.5 K as a function of time after application of a reserve bias voltage. Parameter of the curves is the hydrostatic pressure.

TABLE I. Experimental results for the activation energies,[a] (E_c-E_T), and pressure coefficients $\gamma=(\partial/\partial p)(E_c-E_T)$ of chalcogen centers in Si relative to the conduction-band edge.

Dopant	A level $(D^+\rightarrow D^{2+})$ (E_c-E_T) (eV)	A level γ (10^{-8} meV/Pa)	B level $(D^0\rightarrow D^+)$ (E_c-E_T) (eV)	B level γ (10^{-8} meV/Pa)
S	0.59	-2.05 ± 0.1	0.32	-1.7 ± 0.1
Se	0.52	$-2.1\ \pm0.1$	0.30	-1.8 ± 0.1
Te	0.37	$-1.2\ \pm0.05$	0.19	-0.9 ± 0.05

[a] For the evaluation of the activation energies the temperature dependence of $\sigma(T,0)$ was taken into account only for the *B* levels of S and Se. The activation energies given for the *B* levels of S and Se are thus identical to the changes in enthalpy. The present values for the activation energies are in good agreement with DLTS results given in Refs. 8 and 9.

ifests itself in an exponential transient $\Delta C(t)$ where $\Delta C(t)$ denotes the time-dependent deviation of the space-charge capacitance C from its equilibrium value. The time constant of $\Delta C(t)$ equals[11] the inverse e^{-1} of the thermal emission rate $e(T,p)$, which depends on temperature T and pressure p:

$$e(T,p)\propto\sigma(T,p)T^2\exp[-\Delta G(T,p)/kT]\ , \quad (1)$$

where k is Boltzmann's constant, $\sigma(T,p)$ stands for the capture cross section, and $\Delta G(T,p)=E_c-E_T$ for the change of Gibb's free energy G due to emission of an electron from the deep donor level E_T to the conduction-band edge E_c. From Eq. (1), the pressure coefficient γ of ΔG is

$$\begin{aligned}\gamma&\equiv\frac{\partial\Delta G}{\partial p}\\&=kT\frac{\partial}{\partial p}[\ln e(T,p)-\ln\sigma(T,p)]\ . \quad (2)\end{aligned}$$

Measurements are performed on *p-n* junctions in a He-gas cell developed specially for low-temperature operation[12] with pressures up to 5×10^8 Pa. Results for the normalized capacitance transient $\Delta C(t)/\Delta C(0)$ are given in Fig. 1 for various pressures. Here $\Delta C(0)$ denotes the capacitance amplitude as observed immediately after application of the reverse bias. The emission rate for a specific p and T is obtained from the linear slope of a semilogarithmic $\Delta C(t)/\Delta C(0)$ vs t plot. This slope depends strongly on pressure (see Fig. 1).

For the evaluation of γ from Eq. (2), the pressure dependence of $\sigma(T,p)$ is also required. The capture cross section $\sigma(T,p)$ is obtained from the variation of the capacitance amplitude $\Delta C(0)$ with the time duration of a zero-bias pulse.[13] Within experimental accuracy, no pressure dependence of σ is found for the $D^0\rightarrow D^+$ transition. Electron capture by the *B* centers of S and Se occurs partly through a cascade process, most likely via excited, hydrogen-like states,[8,9] which have negligible pressure coefficients.[14] Since σ is determined by the initial cascade steps, it should also be pressure independent. The capture cross section for the $D^+\rightarrow D^{2+}$ transition exceeds the upper limit of 10^{-15} cm^2 of our experimental setup, the limit being imposed by the finite rise time. The capture cross section of the $D^+\rightarrow D^{2+}$ transition is assumed to be independent of pressure for the evaluation of the pressure coefficient γ from Eq. (2). No temperature dependence of γ is found within the accessible temperature range (typically 40 K in width) for each level.

The experimental results for the pressure coefficient of the trap-binding energy with respect to the conduction-band edge are given in Table I, together with values for the activation energies, as obtained by us from standard deep-level transient spectroscopy (DLTS).[15] The observed pressure coefficients are of the same order of magnitude as the pressure coefficient of the energy gap[16] of -1.5×10^{-8} meV/Pa, but almost 2 orders of magnitude larger than expected from a one-band effective-mass theory for shallow states.[14] The values found for the Te levels are only about half of those obtained for S and Se.

The present experimental results for γ *cannot* be understood within the framework of an effective-mass approximation, even by taking into account contributions from higher conduction bands.[17] The pressure coefficient within such a model is composed from various conduction-band pressure coefficients, weighted by the corresponding densities of states and by squared energy denominators. In Si, the Γ_{15}^c and the L_1^c conduction-band minima move upwards in energy relative to the Δ_1 minimum, with coefficients of 2.1×10^{-8} and 5.3×10^{-8} meV/Pa, respectively, when hydrostatic pressure is applied.[16] The influence of the Γ_{15}^c and higher conduction-band extrema is negligible due to their large energetic separation from the deep-trap level. The pressure coefficient estimated from the contributions of the L_1^c and Δ_1^c minima for deep centers is still very small (-0.1×10^{-8} meV/Pa). This result is clearly in qualitative disagreement with the experimental finding. The multiband character of deep chalcogen traps is thus evident from our data.

From the observation of temperature-independent ground-state binding energies, it was suggested that the chalcogen donor states are pinned to the conduction band.[8,9] The present results using hydrostatic pressure show that such pinning does not occur. Investigations under high pressure are more specific than temperature-induced effects, since in the latter case the conduction bands appear to be shifted uniformly in energy,[18] whereas the pressure coefficients of the individual bands differ in magnitude and sign.[16] Electron-phonon interaction complicates a theoretical discussion of temperature effects considerably.

We interpret our experimental results using the model for deep impurities developed in Refs. 5–7. This model suggests a new classification of impurities: an impurity is defined to be a deep trap theoretically if its central-cell potential alone, without any long-range Coulomb potential, is sufficiently strong to bind a state within the band gap of the host. In contrast to a shallow impurity, such a deep-trap state is localized in real space and is not exclusively derived from the nearest band. Therefore, a trap is experimentally deep if its binding energy changes with respect to a nearby band edge when that edge is perturbed by pressure (or alloying, Ref. 3).

The HVWD model predicts S and Se to be deep, Te to be borderline shallow, and P, As, Sb, Bi to be shallow (see Fig. 3 of Ref. 5 or Fig. 10 of Ref. 6). Using the ten-band LCAO-Koster-Slater scheme of Refs. 5–7, we calculate the pressure dependence of S and Se. The crystal Hamiltonian is represented in an orthogonalized tight-binding function basis, with the nearest-neighbor matrix elements of the host Hamiltonian empirically adjusted to reproduce the principal features of the Si band structure. There are five basis functions per ion (two s, three p orbitals). Interactions beyond nearest neighbors are neglected. Only the short-range part of the impurity potential is taken into account. This central-cell impurity potential is proportional to the difference in the atomic orbital energies.[5-7] The effect of pressure is taken into account by changing[5-7] the nearest-neighbor Hamiltonian matrix elements $M=M_0a^{-2}$ according to their dependence on the lattice constant a. The differences in the on-site diagonal Hamiltonian matrix elements are unchanged. The result is $\partial(E_T-E_v)/\partial p = +1.5\times10^{-8}$ meV/Pa for S as well as for Se. Relative to the conduction-band edge a value of $\gamma=\partial(E_c-E_T)/\partial p = -3\times10^{-8}$ meV/Pa is obtained by including the pressure coefficient of the energy gap,[16] $\partial(E_c-E_v)/\partial p=-1.5\times10^{-8}$ meV/Pa, which is, considering the simplicity of the model, in reasonable agreement with the experimental data of Table I. Generally, the model predicts a weak chemical trend of the pressure dependence of deep traps in Si. The upward shift of the trap level relative to the valence band with pressure reflects the antibonding character of the deep-trap state which is increasingly repelled from the valence (bonding) states.

For P and As, which are predicted to be shallow, the pressure coefficient with respect to the conduction band will be very small according to the one-band effective-mass theory in good agreement with an experimental value of -5×10^{-10} meV/Pa, found for As.[14] For Te the model still predicts an effective-mass-like pressure coefficient, but Te is at the borderline according to the model. Although the model is too crude to yield a quantitative pressure coefficient, the experimental values indicate that Te marks the border between shallow and deep in the theoretically predicted sequence Bi, Sb, As, P, Te, I, Se, S, N, Br, Cl, O, F of substitutional donors in Si.

It is a pleasure to thank B. Skarstam, E. Janzèn, and C. Holm for generously providing the samples. We gratefully acknowledge stimulating discussions with H. J. Queisser, H. G. Grimmeiss, M. Altarelli, P. Wagner, and D. Hochheimer. We thank W. Böhringer and W. Dieterich for expert technical assistance. Work partially supported by Fonds zur Förderung der wissenschaftlichen Forschung, Austria, Project No. 4236.

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[1] M. Jaros, Adv. Phys. 29, 409 (1980); S. T. Pantelides, Rev. Mod. Phys. 50, 797 (1978); H. G. Grimmeiss, Ann. Rev. Mater. Sci. 7, 341 (1977).

[2] H. J. Queisser, in *Festkörperprobleme,* edited by O. Madelung (Vieweg, Wiesbaden, 1971), Vol. 11, p. 45.

[3] D. J. Wolford, W. Y. Hsu, J. D. Dow, and B. G. Streetman, J. Lumin. 18/19, 863 (1979); W. Y. Hsu, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. B 16, 1597 (1977).

[4] Pioneering work on the influence of pressure on S-related levels in Si is due to D. L. Camphausen, H. M. James, and R. J. Sladek, Phys. Rev. B 2, 1899 (1970), who recognized a tendency for smaller pressure coefficients for levels with smaller binding energy. The results for the binding energies and their pressure coefficients do not agree with the present results probably due to a different kind of defect.

[5] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. 44, 810 (1980).

[6] P. Vogl, in *Festkörperprobleme,* edited by J. Treusch (Vieweg, Wiesbaden, 1981), Vol. 21., p. 191.

[7] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow (unpublished).

[8] H. G. Grimmeiss, E. Janzèn, H. Ennen, O. Schirmer, J. Schneider, R. Wörner, C. Holm, E. Sirtl, and P. Wagner, Phys. Rev. B 24, 4571 (1981); H. G. Grimmeiss and B. Skarstam, Phys. Rev. B 23, 1947 (1981).

[9] H. G. Grimmeiss, E. Janzèn, and B. Skarstam, J. Appl. Phys. 51, 4212 (1980); 51, 3740 (1980).

[10] G. W. Ludwig, Phys. Rev. 137, A1520 (1965).

[11] The same method has been developed independently for application to GaAs by R. H. Wallis, A. Zylbersztejn, and J. M. Besson, Appl. Phys. Lett. 38, 698 (1981). In contrast to the present work, the pressure dependence of the capture cross for the deep levels investigated in GaAs could not be determined.

[12] H. D. Hochheimer, Ph.D. thesis, Universität Regensburg, 1973 (unpublished).

[13] A. Zylbersztejn, Appl. Phys. Lett. 33, 200 (1978).

[14] M. G. Holland and W. Paul, Phys. Rev. 128, 30 (1962).

[15] G. L. Miller, D. V. Lang, and L. C. Kimerling, Ann. Rev. Mater. Sci. 1977, 377.

[16] L. R. Saravia, J. Phys. Chem. Solids 35, 1469 (1974).

[17] F. Bassani, G. Iadonisi, and B. Preziosi, Phys. Rev. 156, 735 (1969); Rep. Prog. Phys. 37, 1099 (1974).

[18] R. R. Zucca and Y. R. Shen, Phys. Rev. B 1, 2668 (1970).