Anomalous Electronic Properties of a Hydrogen-Related Deep Donor in c-Si

W. Csaszar and A. L. Endrös

Siemens AG, Corporate Research and Development, 81739 Munich, Germany

The effect of the electric field on the thermal emission rate of electrons from the hydrogen-carbon deep donor level in Si has been investigated by means of double-correlation deep-level transient spectroscopy. The results show for the first time an anomalous strong dependence of the activation energy of a deep level on the electric field to the extent of ≈ 31 meV/10^4 V cm^{-1}. A tentative model is considered which takes into account that the electronic properties of hydrogen depend on its lattice site in the crystal, as predicted by theory. The zero-field activation energy for electrons of the H-C complex was found to be 185 meV.

PACS numbers: 71.55.Ht

The properties of hydrogen in crystalline semiconductors have been studied extensively in the past [1, 2]. The main reason for this interest can be traced to the rich spectrum of interactions of H with impurities and defects in crystalline semiconductors [2]. However, there is insufficient experimental knowledge of the electronic properties of the (isolated) hydrogen species, although several theoretically supported models have been proposed [3–5]. Theory predicts that the charge state of isolated hydrogen [5] as well as of H paired to a group IV impurity in elemental semiconductors [4] depends on its lattice site. The neutral and positively charged H species is supposed to occupy the bond-center site, while negatively charged H enters the interstitial tetrahedral site (T site).

Two defect centers in crystalline silicon are known in the literature that give some experimental evidence for the proposed models and can be used to investigate the main electronic properties of H: The hydrogen-carbon complex [6, 7] and the E3' level [8, 9]. Both centers have been investigated by deep-level transient spectroscopy (DLTS) [10]. The hydrogen-carbon complex [6, 7] acts as a deep donor with an activation energy located about 0.16 eV (low electric field value) below the edge of the conduction band. Because of the isoelectronic behavior of the group IV impurity carbon, which is completely incorporated on substitutional lattice sites in the samples, the H-C complex reflects the principal electronic properties of *hydrogen*. Pseudopotential-density-functional calculations [4] even lead to the surprising result that such an H impurity pair has an energy level that is virtually identical to that of an H atom at the same atomic site but *without* the impurity. The E3' center [8, 9] is regarded by Holm, Bonde Nielson, and Bech Nielsen [8] as involving (most likely isolated) H. This center is metastable and acts as an electron trap located at [8] $E_C - E_T = 0.16 \pm 0.01$ eV after correction of the Poole-Frenkel effect by assuming a Coulomb defect potential [11]. However, no experimental evidence is given for this assumption. Both the E3' center and the H-C complex seem to reflect similar basic properties of H in Si, as can be seen in the corresponding activation energies,

for example. However, the junction electric field apparent in DLTS measurements prevents the correct determination of the activation energy.

In view of this situation, the *zero-field* activation energy of such an H-related center is of considerable interest. It can be determined either by optical methods such as photoluminescence, by Hall effect studies, or by a detailed analysis of the electric field dependence of the activation energy of the deep center by using the double-correlation deep-level transient spectroscopy (DDLTS) principle [12] and extrapolating the data to a zero electric field. The latter option is chosen in this work. An additional question affects the localized potential of the defect, which can also be determined from the results of a detailed electric field study of the activation energy [13]. In line with this it was found to be important to investigate whether tunneling processes are involved in the emission process of charge carriers from the defect center [13, 14].

In this paper, the results of field-dependent measurements of the activation energy of the hydrogen-carbon complex in crystalline *n*-type Si are presented. The zero-field activation energy is found to be 185 meV, which is slightly larger than the low-field value (160 meV) reported in Ref. [6]. It is shown for the first time that this H-related deep center exhibits an anomalous strong field dependence of the emission rate of electrons or its activation energy, and that tunneling is not involved in the emission process. The experimental results are discussed in terms of the three-dimensional Poole-Frenkel effect for three different defect potentials: (1) Coulomb potential, (2) square-well potential, and (3) Gaussian potential. An interpretation of the strong field dependence which takes theoretical calculations of the electronic properties of H in Si into account is discussed.

The samples consist of Czochralski (CZ) and float-zone (FZ) grown Si crystals ([100] oriented) which are doped with phosphorus (shallow dopant) and carbon ($\approx 4 \times 10^{17}$ cm^{-3}). Special care was taken to avoid contamination with metallic impurities by using only materials of the highest available purity. In order to vary the

312

electric field in the observation volume, three different types of samples with different shallow-dopant concentrations are prepared: sample L with $[P] \approx 1 \times 10^{15}$ cm^{-3}, sample M with $[P] \approx 5 \times 10^{15}$ cm^{-3}, and sample H with $[P] \approx 5 \times 10^{16}$ cm^{-3}. The samples are hydrogenized by wet chemical etching at room temperature for 30 s in an acid consisting of HNO_3:HF:CH_3COOH = 5:1:1 [15, 16]. Following this, the polished front surfaces of all samples are supplied with Au-Schottky barriers by evaporating Au onto a substrate at room temperature. Ohmic back contacts are applied by rubbing eutectic GaIn onto the back surface of the samples. The process of sample preparation is described in detail in Ref. [7]. In order to form the H-C complex, the samples were subjected to a reverse-bias annealing (RBA) treatment (-4 V, 320 K, 62 h) [6,7]. The formation of the H-C complex is checked by DLTS measurements before and after the RBA step and was identified by comparing the trap data (position of DLTS peak for equal emission time windows and comparable electric field, concentration, formation and annealing behavior) with the data of Refs. [7]. In Refs. [6] and [7] it was shown that the trap density depends sensitively on the carbon content as well as on the hydrogen content in the samples. For this reason the DLTS peak after the RBA process is correlated with the existence of hydrogen-carbon pairs.

The field-dependent studies of the H-C complex are carried out by means of DDLTS [12]. The crystal orientation of the electric field in the space-charge layer of the Schottky diodes is along a $\langle 100 \rangle$ direction. Only thermal emission processes at a fairly constant electric field strength are studied, thus yielding exponential capacitance transients from which the emission time constants can be directly determined according to

$$C(t) - C_e = \Delta C e^{-t/\tau}, \qquad (1)$$

where $C(t)$ is the capacitance of the DDLTS transient at time t and C_e is the capacitance at the reverse bias applied in the equilibrium state. ΔC is the amplitude of the DDLTS transient. The average electric field strength $\bar{F}$ in a thin slice of the depletion region from which the signal is obtained is calculated [17] from C-V measurements carried out at the corresponding DDLTS temperatures.

In order to check whether tunneling processes are involved in the emission of electrons from the H-C defect center, the emission time constant is measured in the wide temperature range of 44–98 K and at three different electric field strengths. This is done for samples L and H by recording single DLTS transients in a small region (almost homogeneous electric field) of the space-charge layer of the Schottky barriers at a fixed temperature T and directly determining the time constant τ from Eq. (1). The Arrhenius plots in Fig. 1 show the measured emission time constants τ of samples L and H as a function of temperature T. The time constants vary from 2.8 ms to 8.5. h; this allows a very accurate determination
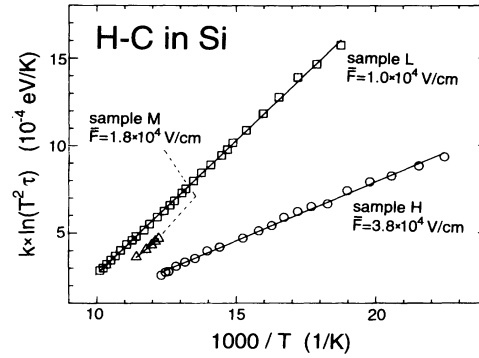

FIG. 1. Arrhenius plots of T^2-corrected thermal emission time constants τ of the H-C complex in the three different samples L (squares), M (triangles), and H (circles). The average electric field $\bar{F}$ is given as a parameter.

of the activation energies. The Arrhenius plot of sample M in the temperature range of 82–88 K, which was recorded via a conventional DLTS measurement, is also drawn. For the evaluation of the activation energies from the slope of each Arrhenius plot in Fig. 1, the capture cross section was assumed to be independent of temperature. This is proven by measurements of Heyman, Endrös, and Haller [18] which show that the capture cross section of the H-C complex varies only by a factor of 2 within the considered temperature interval. This leads to an error in the determination of the activation energy of only a few meV in the case of the H-C complex. Table I clearly indicates that the activation energy of the H-C complex is field dependent.

Halder and Barnes [19] and Vincent, Chantre, and Bois [13] showed that phonon-assisted tunneling of electrons between the potential well and the conduction band leads to a nonlinear Arrhenius plot. This is also true when a pure tunneling process as described by Korol [20] is dominant. In this case the emission rate becomes independent of temperature. However, it can be seen in Fig. 1 that the Arrhenius equation of the H-C complex is strongly linear, which means that the pairs of values (T, τ) obey the Shockley-Read-Hall statistics [21]. Consequently, neither phonon-assisted tunneling nor pure tunneling takes place in the process of electron emission from the H-C defect center in the investigated range of temperature and electric field.

TABLE I. Electric field ($\bar{F}$)-dependent activation energy E_A of the H-C complex of samples L, M, and H; also shown is the value of E_A of earlier measurements [6].

	From Ref. [6]	Sample L	Sample M	Sample H
$\bar{F}$ (V/cm)	8×10^3	1.0×10^4	1.8×10^4	3.8×10^4
E_A (meV)	160 ± 2	154 ± 1	134 ± 5	67 ± 1

To obtain a detailed description of the field dependence of the activation energy of the hydrogen-carbon complex, sample H is investigated by the DDLTS principle [12]. It is found that the emission rates depend strongly on the electric field and that the field effect increases with decreasing temperature. The activation energy of the H-C complex at each electric field is deduced from the slope of the Arrhenius plots similar to Fig. 1. The results show (Fig. 2) that a good linear correlation (99.8%) exists between the activation energy E_A and the electric field F. By extrapolating the data to $F = 0$ we observe that the zero-field activation energy of the H-C complex equals 185 meV (± 5 meV).

For various deep-level centers in semiconductors, like the thermal donors [22], Te [23,24], S [24], and Se [24,25] in silicon, Au, Cu, and Ag in ZnTe [26] and the 0.85 eV hole level in GaP [27], the model of the one-[28] or three-dimensional [11] Poole-Frenkel effect with a Coulomb defect potential shows good agreement with the experimental data. For this reason we also tried to use the three-dimensional model by Hartke [11] to explain the field dependence of the H-C complex. However, it can be seen in Fig. 2 that such a model cannot be reconciled with our experimental results by a long way. The observed field dependence (≈ 31 meV/10^4 V cm^{-1}) is much stronger than that predicted by the model of Hartke (≈ 6 meV/10^4 V cm^{-1}). The strongest field dependence reported in the literature was observed for Cr [13] and the $E3$ level [14] in GaAs and for the $E1$ level [19] in Al$_{0.5}$Ga$_{0.5}$As. But in all three cases *phonon-assisted tunneling* played a dominant role in the emission process.

However, it can be excluded that tunneling processes are involved in the emission process of electrons from the H-C complex; i.e., no level is reported in the literature which comes close to the field dependence of the activation energy of the H-C center in Si.

Since the Coulomb potential was found to be unsuitable for describing the experimental results, we tried to fit our data to Poole-Frenkel emission from other three-dimensional defect potentials, namely, a square-well potential and a Gaussian potential. Such potentials are characterized by a range that can be varied in the fitting procedure. The best fits (Fig. 2) that can explain the experimental data are gained for a square-well potential with radius $r = 37$ nm and for a Gaussian potential with an amplitude $V_0 = 185$ meV and a characteristic width α of 21.5 nm. However, if we compare the range of our fit potentials (37 and 21.5 nm) with the lattice constant of Si (0.54 nm) we see that such long-range defect potentials may only be considered if we deal with large defects, i.e., defects involving typically more than ten lattice sites, but not with point defects as for a hydrogen atom (a single proton) bound to carbon. For this reason the H-C complex is expected to have a potential with a range in the order of a few nanometers as a Coulomb potential or other [27,29,30] defect potentials found for point defects in semiconductors. We conclude that the standard theories used to describe the field-enhanced emission of charge carriers from deep levels, namely, the Poole-Frenkel model and the quantum-mechanical tunneling model, cannot satisfactorily explain the experimental data of the H-C complex [31].

The following tentative model is proposed, in which the observed properties of the H-C center are explained within the scope of the present theory of the behavior of hydrogen in semiconductors. There is theoretical conformity that the charge state of H as well as its *electronic properties* are expected to depend on its lattice position in the semiconductor crystal [32] although direct experimental evidence is still lacking. For H$^+$ the bond-centered interstitial (BC) site is recognized to be the stable position [5]. Applied to the H-C complex, the equilibrium position of H$^+$ for a zero electric field is the BC site between a Si atom and a substitutional C atom. Because of the electric field in the space-charge layer of the samples, however, the position H$^+$ is altered in line with the electric field strength. According to the calculations of Denteneer, Van de Walle, and Pantelides [4] this is accompanied by a change of its electronic properties, i.e., the energetic position of the H$^+$/H^0 defect level in the Si bandgap is changed. Consequently, the field dependence of the H-C activation energy of ≈ 31 meV/10^4 V cm^{-1} is the sum of two effects: (1) a contribution of ≈ 6 meV/10^4 V cm^{-1} which is caused by the field-enhanced emission of electrons described by the Poole-Frenkel model with a Coulomb defect potential due to the ionized center being a proton and (2) a structural term to
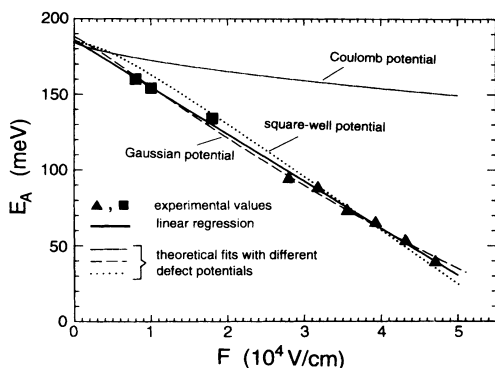

FIG. 2. Electric field (F) dependence of the DLTS activation energy E_A of the H-C complex in Si. Triangles and squares: experimental values measured by the DDLTS principle (triangles) and taken from Table I (squares). The solid line represents the computed linear regression between E_A and F: $E_A = -31$ (meV/10^4 V cm^{-1}) $\times F + 185$ meV. Other curves: theoretical fits with the three-dimensional Poole-Frenkel model ($T = 70$ K) using a Coulomb potential (dash-dotted line), a square-well potential of radius 37.0 nm (dotted line), and a Gaussian potential with an amplitude of 185 meV and a characteristic width of 21.5 nm (dashed line).

the extent of ≈ 25 meV$/10^4$ V cm^{-1} which results from the position-dependent electronic properties of hydrogen.

In summary, it has been shown that the H-C complex in crystalline Si, which reflects the principal properties of H, has a zero-field activation energy of 185 meV for electrons. The anomalous strong field dependence of ≈ 31 meV$/10^4$ V cm^{-1} of the activation energy for electrons cannot be satisfactorily understood in terms of the Poole-Frenkel effect assuming different defect potentials, nor in terms of the quantum-mechanical tunneling model. A tentative model that takes the dependence of the electronic properties of H on its lattice site into account has been presented and can be understood in terms of theoretical predictions.

[1] S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A **43**, 153 (1987), and references therein.

[2] E. E. Haller, Semicond. Sci. Technol. **6**, 73 (1991), and references therein.

[3] P. Deák, L. C. Snyder, and J. W. Corbett, Phys. Rev. B **37**, 6887 (1988).

[4] P. J. H. Denteneer, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. Lett. **62**, 1884 (1989).

[5] C. G. Van de Walle et al., Phys. Rev. B **39**, 10791 (1989).

[6] A. Endrös, Phys. Rev. Lett. **63**, 70 (1989).

[7] A. L. Endrös, W. Krühler ,and F. Koch, J. Appl. Phys. **72**, 2264 (1992).

[8] B. Holm, K. Bonde Nielsen, and B. Bech Nielsen, Phys. Rev. Lett. **66**, 2360 (1991).

[9] K. Irmscher, H. Klose, and K. Maass, J. Phys. C **17**, 6317 (1984).

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

[11] J. L. Hartke, J. Appl. Phys. **39**, 4871 (1968).

[12] H. Lefèvre and M. Schulz, Appl. Phys. **12**, 45 (1977).

[13] G. Vincent, A. Chantre, and D. Bois, J. Appl. Phys. **50**, 5484 (1979).

[14] S. Makram-Ebeid, Appl. Phys. Lett. **37**, 464 (1980).

[15] A. J. Tavendale, A. A. Williams, and S. J. Pearton, Mat. Res. Soc. Symp. Proc. **104**, 285 (1988).

[16] C, H. Seager, R. A. Anderson, and J. K. G. Panitz, J. Mater. Res. **2**, 96 (1987).

[17] S. M. Sze, Semiconductor Devices, Physics and Technology (John Wiley & Sons, New York, 1985), p. 163.

[18] J. Heyman, A. L. Endrös, and E. E. Haller (unpublished).

[19] N. C. Halder and D. E. Barnes, J. Vac. Sci. Technol. B **10**, 94 (1992).

[20] E. N. Korol, Sov. Phys. Solid State **19**, 1327 (1977).

[21] W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

[22] L. C. Kimerling and J. L. Benton, Appl. Phys. Lett. **39**, 410 (1981).

[23] K. Hofmann and M. Schulz, Appl. Phys. A **33**, 19 (1984).

[24] G. Pensl et al., in Defects in Semiconductors, Materials Science Forum, Vols. 10–12, edited by H. J. von Bardeleben (Trans Tech Publications Ltd., Aedermannsdorf, Switzerland, 1986), pp. 911–916 .

[25] H. Pettersson and H. G. Grimmeiss, Phys. Rev. B **42**, 1381 (1990).

[26] J. L. Pautrat, Solid State Electron. **23**, 661 (1980).

[27] N. Baber and M. Zafar Iqbal, J. Appl. Phys. **62**, 4471 (1987).

[28] J. Frenkel, Phys. Rev. **54**, 647 (1938).

[29] N. Baber et al., Phys. Rev. B **45**, 4043 (1992).

[30] Q. S. Zhu et al., J. Appl. Phys. **73**, 771 (1993).

[31] Irmscher, Klose, and Maass (Ref. [9]) made a quantitative estimate of the three-dimensional Poole-Frenkel effect of the $E3'$ center. The results indicate a stronger field dependence of the activation energy than is expected for a Coulomb defect potential of a single ionized center.

[32] C. G. Van de Walle, in Hydrogen in Semiconductors, Semiconductors and Semimetals Vol. 34, edited by J. I. Pankove and N. M. Johnson (Academic, New York, 1991), pp. 600–614, and references therein.