Negative-*U* Properties for Interstitial Boron in Silicon

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Electrical detection of a single donor level of interstitial boron at $E_c - 0.13$ eV using novel photo–deep-level transient spectroscopy techniques is reported. Complementary behavior between this level and the acceptor level at $E_c - 0.45$ eV establishes that the defect levels have negative-U ordering. The donor level exhibits a large Poole-Frenkel effect which, when properly accounted for, provides a direct and unambiguous connection to the EPR-identified interstitial boron atom. This represents the first definitive indentification of negative-U properties for a defect in any solid.

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A defect has negative-U^{1-3} properties if it can trap two electrons with the second bound more strongly than the first. It is as if there were a net attraction between the two carriers (negative Hubbard correlation energy[4]). In this Letter, we present what we believe is the first definitive and unambiguous demonstration of negative-U properties for a defect in any solid. The defect is *interstitial boron in crystalline silicon,* a simple point defect produced by electron irradiation at cryogenic temperatures of boron-doped silicon.[5]

The electrical level structure that we determine for the defect is summarized in Fig. 1(a). There are two levels in the gap with an acceptor level (−/0) at $E_c - 0.45$ eV and a donor level (0/+) at $E_c - 0.13$ eV. This inverted ordering implies a negative effective U, with the neutral B_i^0 state thermodynamically unstable.

The suggestion that interstitial boron might have negative-U properties, with a level structure similar to that of Fig. 1(a), has been made previously.[6,7] The evidence cited was as follows: (1) EPR studies[5] indicated three charge states in the gap, B_i^+, B_i^0, B_i^-, the metastable EPR-active neutral state being seen only after photogeneration. (2) Decay of the photogenerated B_i^0 EPR signal (~15 min at 50 K) was interpreted as thermally activated electron emission

$$B_i^0 \rightarrow B_i^+ + e^-, \qquad (1)$$

indicating a donor level at $\sim E_c - 0.15$ eV.[5] (3) Deep-level transient spectroscopy (DLTS) junction capacitance studies[6,7] failed to detect this donor emission, however, detecting only a single deeper level at $E_c - 0.45$ eV, as shown in Fig. 1(c). This was interpreted as a two-stage electron emission,

$$B_i^- \rightarrow B_i^0 + e^- \rightarrow B_i^+ + 2e^-, \qquad (2)$$

a single DLTS peak being observed at $E_c - 0.45$ eV because the limiting process is the first deeper electron emission, the second electron following immediately. Indirect evidence was cited to support the two-electron emission model by comparison of the DLTS peak amplitude to other related DLTS peaks.

In the present Letter we report direct electrical detection of the single-donor electron emission at $E_c - 0.13$ eV, providing a critical electrical test of the negative-U ordering. A detailed kinetic study of the decay of the photogenerated EPR study is also reported which allows unambiguous identification of the negative-U electrical levels with interstitial boron.

First, we show in Fig. 1(b) the results for the

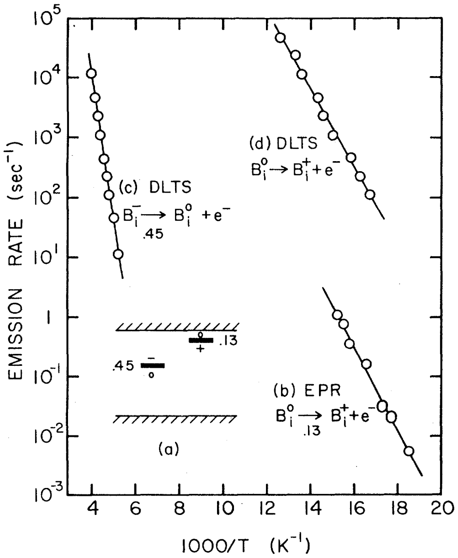

FIG. 1. (a) Electrical level structure for interstitial boron. (b) Decay rate for the metastable B_i^0 EPR spectrum. (c) DLTS emission rate from the $E_c - 0.45$ eV level. (d) DLTS emission rate from the $E_c - 0.13$ eV level observed in the presence of light.

photogenerated B_i^0 EPR signal decay. In this study a p-type sample ($B \sim 1.5\times 10^{16}$ cm^{-3}), previously made high resistivity by prolonged electron irradiation ($\sim 10^{18}$ e/cm^2) and room-temperture anneal, was reirradiated by 2.5-MeV electrons ($\sim 10^{17}$ e/cm^2) *in situ* at 20.4 K, to produce interstitial boron. The observed decay is given by

$$\tau_{\text{EPR}}^{-1} = 6.8\times 10^{10} \times \exp[-(0.14\pm 0.01 \text{ eV})/kT] \text{ sec}^{-1}. \qquad (3)$$

Correction for the T^2 dependence of the conduction-band thermal velocity and density of states leads to an estimate of the donor position at $E_c - 0.13\pm 0.01$ eV.

For the electrical DLTS measurements, either diffused p^+n diodes processed from counterdoped n-type ($P\sim 3\times 10^{16}$ cm^{-3}, $B\sim 1\times 10^{16}$ cm^{-3}) pulled silicon, or chrominum Schottky barrier diodes processed from p-type ($B\sim 1.5\times 10^{15}$ cm^{-3}) vacuum floating-zone silicon were used. All diodes were fabricated in a mesa configuration to allow optical access to the junction region from the side of the diode. The n-type samples were irradiated with 1.5-MeV electrons and the p-type samples with 2.4-MeV electrons, both *in situ* at 4.2 K, to produce interstitial boron for study.

The failure to detect the $E_c - 0.13$ eV level in the previous DLTS studies can be understood as follows: In the normal DLTS experiment, each electron-trap-filling pulse will convert some interstitial boron atoms to the negative charge state. Since the deeper (0.45 eV) B_i^- state cannot emit at the low temperature required to observe the B_i^0 donor level emission, these negatively charged centers are essentially removed from the experiment. With the repetitive pulses required by DLTS, all of the centers will rapidly accumulate in the negatively charged state, leaving none in the neutral state to observe.

We have avoided this accumulation by illuminating the diode with $0.3 \text{ eV} \leq h\nu \leq 1.1$ eV light (tungsten source through a room-temperature silicon filter and a Pyrex window on the cryostat), to ionize B_i^-,

$$B_i^- \xrightarrow{h\nu} B_i^0 + e^-. \qquad (4)$$

This temperature independent photo-induced decay can be monitored after each trap-filling pulse by the corresponding transient capacitance change. The light level was adjusted to give a photo decay time short with respect to the period between trap-filling pulses. This assures that no B_i^- is present at the beginning of each pulse. The result is shown in Fig. 2(a). In the presence of the light, a new peak is observed, and in the approximate temperature range expected. This new peak disappears in a 1:1 correspondence with the $E_c - 0.45$ eV DLTS peak during either thermal annealing at ~ 240 K or minority carrier injection annealing at 78 K, confirming that the two levels are associated with the same defect.

The negative-U ordering of the two levels can now be tested by the dependence of the amplitudes of the two related capacitance transients versus the trap-filling pulse width. This is shown in Fig. 2(b). The shallow new peak decreases in amplitude as the pulse width increases, an anomalous result for a normal level. At the same time, the amplitude of the photo-induced B_i^- decay increases. In Fig. 2(b) we have plotted one half of the B_i^- decay amplitude because it is a two-electron decay, Eq. (2). This complementary 1:1 behavior between the two transient decays, and the constancy of the sum of their amplitudes, provide a direct and unambiguous demonstration that the two levels belong to the same defect and must be in inverted negative-U ordering.

Finally, we provide direct confirmation that the

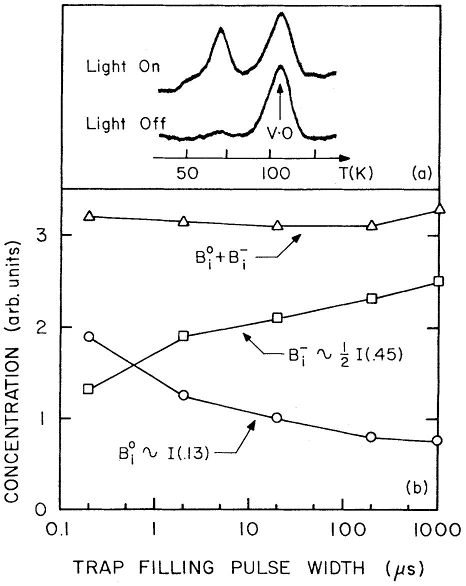

FIG. 2. (a) New DLTS peak observed with simultaneous photoexcitation. The peak at ~105 K arises from the vacancy-oxygen pair, also present. (b) Concentration of B_i^0 and B_i^- at the end of each trap-filling pulse as deduced from the amplitudes (I) of the corresponding DLTS transients.

negative-U levels being studied by DLTS arise from interstitial boron. In Fig. 1(d) we show the emission rate versus temperature measured for the shallow level in the DLTS experiments of Fig. 2. Although the level position inferred from the slope of the curve (0.12 eV) is in reasonable agreement with the EPR results of Fig. 1(b) (0.13 eV), there is an unacceptable factor of 10^3 difference in the emission rates.

We find that this discrepancy results from an enhancement of the emission rate by the electric fields in the depletion region of the DLTS diode. This is the Poole-Frenkel effect,[8, 9] where the barrier for emission from a Coulomb attractive center is lowered by an amount

$$\Delta E_B = e(e/\pi\epsilon\epsilon_0)^{1/2}\mathcal{E}^{1/2} = \beta\mathcal{E}^{1/2}. \qquad (5)$$

Here $\mathcal{E}$ is the electric field, e the electronic charge, ϵ the dielectric constant of the material, and ϵ_0 the permittivity of free space. The analysis of Frenkel predicts for the emission rate[8, 9]

$$\ln e_n(\mathcal{E}, T) = \ln e_n(0, T) + (\beta/kT)\mathcal{E}^{1/2}. \qquad (6)$$

To study this, we have used Schottky p-type diodes where we find that the B_i^0 emission can also be observed in DLTS studies by using optical trap-filling pulses (provided by a Strobotac synchronized with the DLTS spectrometer). The diodes were first characterized by C-V measurements at the temperature of the DLTS studies so that the electric field in the junction could be determined in terms of the applied reverse bias. The field varies linearly from a maximum at the junction to zero at the termination of the depletion region. In order to have a well defined electric field, therefore, the pulse sequence illustrated in the inset of Fig. 3 was used. During the optical pulse (i), a small reverse bias was applied in order to allow only levels near the junction to be filled. Immediately after the pulse (ii), additional reverse bias was applied providing a narrow range of electric fields to the emitting levels, as shown, the average of which could be varied by the applied reverse bias.

The emission rates observed at various average electric fields are shown in Fig. 3, plotted as $\ln e_n$ vs $\mathcal{E}^{1/2}$ at 65 K. The solid straight line, representing the $\mathcal{E}^{1/2}$ dependence predicted by Eq. (6), clearly extrapolates within the accuracy of the measured points to the EPR value, also shown. This provides unambiguous identification of the level as arising from interstitial boron. In addition, the large, quantitatively demonstrated Poole-Frenkel effect[10] confirms the single-donor character of the level inferred by this identification.

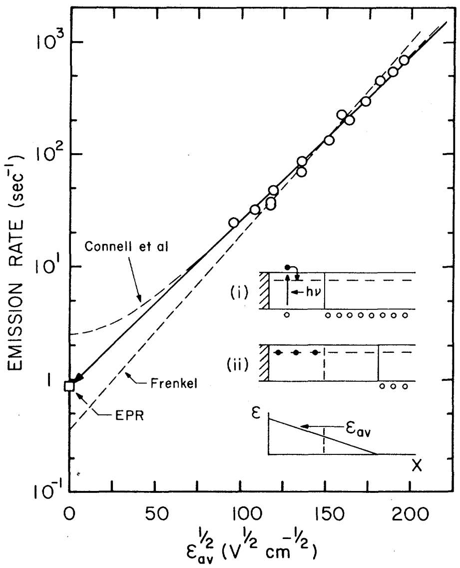

FIG. 3. Dependence of the electron emission rate from neutral interstitial boron on the electric field in the junction at 65 K. The insets show the bias conditions used to obtain a well-defined electric field in the diode junction during emission (see text).

We note parenthetically that the slope of the line drawn in Fig. 3 corresponds to a value for β which is 15% smaller than that given by Eq. (5). While this is within the accuracy of our estimates of $\mathcal{E}$ from the C-V measurements, we do not necessarily anticipate exact agreement with Eq. (5). In particular, others[11-13] have derived somewhat different forms by extending Frenkel's derivation from one to three dimensions. For comparison we have also shown in Fig. 3 best matches to the predictions of Frenkel [Eq. (6)] and Connell, Comphausen, and Paul[13] plotted using the theoretical value for β [Eq. (5)]. The experimental accuracy is not sufficient to judge the merits of either model but it is interesting that they straddle the EPR result.

In conclusion, we have demonstrated that interstitial boron in crystalline silicon has negative-U properties, its acceptor level at $E_c - 0.45$ eV lying inverted below its donor level at $E_c - 0.13$ eV. The effective electron-electron binding energy for two electrons at the defect is therefore 0.32 eV. We believe this is the first identified defect in any solid which has been demonstrated to have this remarkable property.

It has also been suggested that the isolated lattice vacancy in silicon should have negative-U

properties,[14] and experimental evidence has been cited as tentative confirmation.[7] However, a critical and definitive test of this suggestion, such as that presented in the present Letter for interstitial boron, has yet to be successfully accomplished. Work is in progress in our laboratory to attempt this more difficult test as well.

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[1] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[2] R. A. Street and N. F. Mott, Phys. Rev. Lett. 35, 1293 (1975).

[3] M. Kastner, D. Adler, and H. Fritzche, Phys. Rev. Lett. 37, 1504 (1976).

[4] J. Hubbard, Proc. Roy. Soc. London, Ser. A 276, 238 (1963).

[5] G. D. Watkins, Phys. Rev. B 12, 5824 (1975).

[6] G. D. Watkins and J. R. Troxell, Phys. Rev. Lett. 44, 593 (1980).

[7] J. R. Troxell and G. D. Watkins, Phys. Rev. B 22, 921 (1980).

[8] J. Frenkel, Tech. Phys. USSR 5, 685 (1938).

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

[10] Note in Fig. 3 that even at the lowest fields attainable (10^4 V/cm for 1 V reverse bias, on diodes with net acceptor concentrations $\sim 6.9\times 10^{14}$ cm^{-3} after irradiation), the emission rate is still enhanced by ~ 30. It is interesting therefore that this very large effect has been noted in only a few very recent DLTS studies [L. C. Kimerling and J. L. Benton, Appl. Phys. Lett. 39, 410 (1981); C. E. Jones and G. E. Johnson, J. Appl. Phys. 52, 5159 (1981)].

[11] A. K. Jonscher, Thin Solid Films 1, 213 (1967).

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

[13] G. A. N. Connell, D. L. Camphausen, and W. Paul, Philos. Mag. 26, 541 (1972).

[14] G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. Lett. 43, 956 (1979).

Electric Field Dependence of Crystallinity in Poly(Vinylidene Fluoride)

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It is shown that the crystallinity of poled films of poly(vinylidene fluoride) can be changed by the application of an electric field. This is the first time that electric-field–induced changes of crystallinity in a polymer have been reported, and this observation confirms the hypothesis that reversible changes in crystallinity with temperature contribute significantly to the pyroelectric effect in poly(vinylidene fluoride).

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Recently, it has been recognized that poly(vinylidene fluoride) and some vinylidene fluoride copolymers are ferroelectric. This discovery has stimulated a large amount of research since ferroelectricity had not been observed previously in polymers.[1-3] Much of this work has been devoted to explaining the origin and the magnitude of the pyroelectric effect.

In this paper, we report the observation of electric-field–induced changes of crystallinity in poly(vinylidene fluoride). We show that this observation confirms our earlier speculation[4,5] that a reversible temperature dependence of the crystallinity contributes significantly to the pyroelectric effect in poly(vinylidene fluoride). The fact that reversible changes in crystallinity can contribute to the pyroelectric effect has not been recognized previously, nor have electric-field–induced changes in crystallinity been observed.

Poly(vinylidene fluoride) is a crystalline polymer with a crystallinity χ_c of about 0.5; that is, about half of the molecules are in the crystalline phase. In the planar zigzag configuration, the β phase, the crystalline region is strongly polar. If the polarization axes of the crystalline regions are aligned by the application of a high electric field, referred to as a poling process, the polarization P of a sample is $\chi_c P_c$ where P_c is the polarization of the crystalline phase. Therefore, pyroelectricity, the change in sample polarization caused by a change in temperature, can arise not only from changes in the temperature dependence