Negative-U Properties for Point Defects in Silicon

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Experimental evidence is presented in support of a recent suggestion by Baraff, Kane, and Schlüter that the isolated lattice vacancy in silicon is an Anderson negative-U system. The second donor level (+/++) (of charge state +, if defect level is occupied by an electron; ++, if unoccupied) is located at $E_v + 0.13$ eV, above a first donor level (0/+) at $\sim E_v + 0.05$ eV. Evidence is presented that interstitial boron has negative-U properties with a single donor level (0/+) at $\sim E_c - 0.13$ eV, above a single acceptor level (-/0) at $E_c - 0.45$ eV.

In 1975, Anderson[1] proposed that the failure to detect paramagnetism for intrinsic defects in chalcogenide glasses could be explained if there existed an effective negative correlation energy U for electrons trapped at the defects. Anderson suggested that the energy gain associated with electron pairing in the dangling bonds of a defect, and coupled with a large lattice relaxation, might overcome the Coulombic repulsion of the two electrons, supplying a net effective attractive interaction between the electrons (negative U) at the site. Electrons would therefore be trapped by pairs at the defect, providing no paramagnetism. Since that time, other microscopic models have been suggested where change of defect bonding coordination could supply the driving force.[2] It is now generally accepted that such a phenomenon is probably the correct explanation for the properties of these glasses. However, to our knowledge there has been no direct microscopic experimental confirmation that any defect with such a property actually exists in a solid.

In this Letter we present evidence that two well-characterized simple point defects in crystalline silicon have this property. They are the isolated lattice vacancy and interstitial boron, both common defects produced by electron irradiation.

The possibility that the silicon lattice vacancy has a negative U was first suggested recently by Baraff, Kane, and Schlüter[3] on the basis of theoretical calculations. They concluded that a second donor level $(+/++)$[4] is stable in the forbidden gap but that the first donor level $(0/+)$ is below it as a result of the larger Jahn-Teller relaxation for the neutral defect. (Experimentally it has been established[5] that both V^+ and V^0 undergo a tetragonal Jahn-Teller distortion with the V^0 Jahn-Teller energy being approximately four times that for V^+.) This is illustrated in Fig. 1(a), the electrical level positions indicated being those which we determine from the data to be described in this Letter. In Fig. 1(b), we show the corresponding level diagram which we propose for interstitial boron. Here a single acceptor level $(-/0)$ at $E_c - 0.45$ eV lies, inverted, below the single donor state $(0/+)$ at $\sim E_c - 0.13$ eV.

Consider first the vacancy. The inverted level order implies that V^+ is a *metastable* state, with the reaction

$$2V^+ \rightarrow V^0 + V^{++} \quad (1)$$

lowering the energy of the system. Consistent with this, V^+, which can be studied by EPR, is seen only by photoexcitation at cryogenic temperatures.[5,6] The kinetics of the V^+ decay after the light is turned off reveals an activation energy of 0.057 ± 0.004 eV which can be interpreted[5,6] as

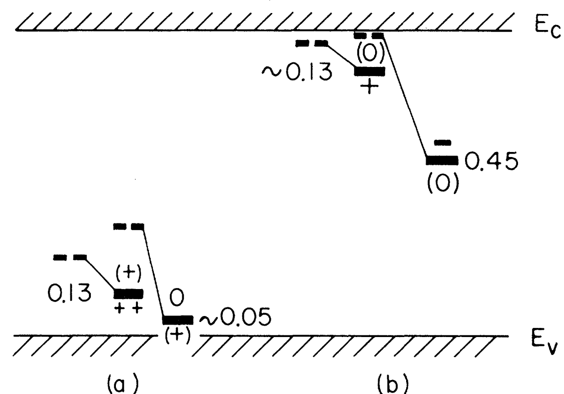

FIG. 1. (a) Suggested level positions for the isolated vacancy. Greater Jahn-Teller relaxation for the V^0 state causes a level inversion with the first donor state (0/+) below the second (+/++). (b) Suggested level positions for interstitial boron. Change of lattice configuration as the charge state changes from $B_i^+ \rightarrow B_i^0 \rightarrow B_i^-$ causes level inversion with the acceptor level (-/0) below the donor (0/+). The dashed lines indicate schematically the level positions before lattice readjustment. Level positions (in electronvolts) are denoted from the nearest band edge.

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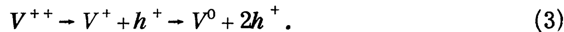
the thermally activated hole release

$$V^+ \to V^0 + h^+, \qquad (2)$$

locating the donor state at $\sim E_v + 0.05$ eV.

The level at $E_v + 0.13$ eV has been observed in deep-level capacitance transient spectroscopy (DLTS).[6-8] The assignment in Fig. 1(a) as the second donor state implies a two-stage hole emission in the DLTS experiment:



$$V^{++} \to V^+ + h^+ \to V^0 + 2h^+. \qquad (3)$$

Normally one would expect to detect each hole emission separately in a DLTS study as the temperature is scanned because, for a normal defect, a hole is bound progressively more strongly as other holes are removed, requiring successively higher temperatures for each ionization event. However, for the inverted negative-U order of Fig. 1(a), the hole involved in the first ionization is bound more strongly (0.13 eV) than the second (0.05 eV) and, at a temperature where the first hole is emitted, the second hole should follow immediately. Therefore, in the DLTS experiment, only a single peak should be observed, reflecting the level at $E_v + 0.13$ eV, but its amplitude should be a factor of 2 larger than normal.

This, therefore, is a unique feature of a negative-U system and serves as a critical test. In order to make this on the vacancy, we need an independent estimate of the vacancy concentration. This has been achieved in the following way: A p-type floating-zone sample (B concentration $\sim 10^{16}$ cm^{-3}) was doped in growth with $\sim 10^{18}$ Sn atoms/cm^3. From EPR studies in this material, it has been established that the Sn atom is an effective vacancy trap, the Sn-vacancy pair produced when the vacancy anneals giving a distinctive EPR spectrum.[9] In DLTS studies on an irradiated n^+/p diode fabricated from this material, we find that as the vacancy level at $E_v + 0.13$ eV disappears upon annealing, two new levels, identified as associated with the Sn-V pair[10] at $E_v + 0.07$ and $E_v + 0.32$ eV emerge. The amplitudes of these two DLTS peaks are always equal but each is 0.50 ± 0.05 that of the $E_v + 0.13$ eV vacancy level. We expect the conversion to Sn-V pairs to be nearly 100% because at a concentration of $\sim 10^{18}$ cm^{-3}, tin should be the dominant vacancy trap. This is confirmed by an increase of a factor of 50 in the vacancy annealing rate in the tin-doped material over that in the corresponding undoped material at a given temperature. We interpret this therefore to indicate that for the Sn-V pair, the two levels are probably the single- and double-donor states, in their *normal* order, and we are detecting single-hole emission from each. (From EPR studies[9] it has been determined that the neutral Sn-V pair has a different configuration from that for the neutral isolated vacancy, with no Jahn-Teller distortion, consistent with an uninverted order.) The fact that the DLTS peak for the $E_v + 0.13$ eV level of the vacancy is twice as intense therefore provides confirmation that it is the second donor state and that the level order is inverted.

This model also provides a simple explanation for the observation that vacancies remove holes in p-type material,[8,11,12] a fact which has been difficult to understand if the $E_v + 0.13$ eV level were an acceptor state in normal order above the $E_v + 0.05$ eV donor level.[6]

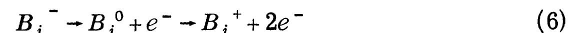
For interstitial boron, the inverted order of Fig. 1(b) implies that B_i^0 is unstable, the reaction

$$2B_i^0 \to B_i^+ + B_i^-, \qquad (4)$$

lowering the energy of the system. Again, as for V^+, B_i^0 has been seen by EPR only after photoexcitation.[13] The decay of the EPR signal after photoexcitation reveals an activation energy of ~ 0.13 eV, which in the model of Fig. 1(b) locates the donor level at $\sim E_c - 0.13$ eV, the decay reflecting[13]

$$B_i^0 \to B_i^+ + e^-. \qquad (5)$$

In the DLTS studies, only one level is observed at $E_c - 0.45$ eV.[14] The level at $E_c - 0.13$ eV is not observed. This can be explained in the level scheme of Fig. 1(b) where, as for the vacancy, the two-stage ionization



$$B_i^- \to B_i^0 + e^- \to B_i^+ + 2e^- \qquad (6)$$

is again limited by the first ionization event (0.45 eV), the second (0.13 eV) following immediately. Again only one DLTS peak will be observed reflecting the $E_c - 0.45$ eV level, but its amplitude should again be a factor of 2 larger.

This has been tested in the following experiment: Asymmetric p^+/n diodes were fabricated on n-type pulled silicon partially counterdoped with boron (3×10^{16} P/cm^3; 1×10^{16} B/cm^3). For 1.5-MeV electron irradiation at 4.2 K the primary damage products should be equal concentrations of simple lattice vacancies and interstitial silicon atoms. From EPR studies it has been previously concluded that the interstitial silicon atoms are unstable, migrating at ~ 4.2 K to be trapped by substitutional boron atoms to

produce interstitial boron atoms.[13] This is confirmed in the DLTS studies were we see the $E_c - 0.45$ eV interstitial boron peak after 4.2-K irradiation. After the 100-K anneal, where vacancies are known to migrate, we see the emergence of V-O pairs [at $E_c - 0.16$ eV (Refs. 7 and 10)] and V-P pairs [at $E_c - 0.43$ eV (Refs. 7 and 10)]. If we assume that the V-O and V-P pairs account for all of the original vacancies, the concentration of interstitial boron should be equal to the sum of the V-O and V-P pairs. We find, however, that the amplitude of the B_i DLTS peak is, within experimental accuracy, exactly twice the sum of the amplitudes of the V-O and V-P pairs (normal single-charge-emitting levels), providing confirmation to the negative-U model of Fig. 1(b).

Another indication that the necessary large electron-lattice coupling exists at each of these defects is the observation that both the vacancy and interstitial boron display greatly enhanced annealing rates under minority-carrier–injection conditions.[6,14,15] This necessarily means that the electronic energy available upon electron and/or hole capture at the defect is being efficiently converted into local lattice motion and/or atomic rearrangement.

In the case of interstitial boron, a detailed study of the injection-enhanced annealing has provided additional insight into the microscopic structure of the defect in its different charge states. In particular, we find that the enhancement in both n- and p-type materials is proportional to the square of the injected current density. This is an uncommon observation and implies that capture of two minority carriers, and therefore a change in charge state of two,

$$B_i^+ \rightleftarrows B_i^0 \rightleftarrows B_i^-, \tag{7}$$

is required for stimulated defect migration. Since this is observed in both n- and p-type materials, we conclude that the complete charge-state change *cycle* is required for motion. This in turn implies a *Bourgoin*[16] mechanism in which the configuration of the atom changes, the B_i^+ configuration being the saddle point for migration between two B_i^- configurations and vice versa. In a forthcoming paper,[14] we will describe several possible microscopic models, deduced from the EPR studies of B_i^0, which could be involved. The important point that we would like to make here is that for interstitial boron, we can conclude from these studies that the driving force for negative-U behavior is the change in its microscopic lattice configuration.

In summary, we have presented evidence that both the lattice vacancy and interstitial boron have negative-U properties in crystalline silicon. For the vacancy, the required electron-lattice coupling derives from the Jahn-Teller relaxation, with no change in defect symmetry. This, therefore, provides an example of the mechanism originally proposed by Anderson.[1] The other, interstitial boron, appears to be driven by a change in lattice configuration with charge state. This aspect has certain features in common with "valence-alternation-pair" model suggested by Kastner, Adler, and Fritzsche.[2] Experiments are being continued to test these ideas further.

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Spin-Glass–Ferromagnetic Multicritical Point in Amorphous Fe-Mn Alloys

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The ac susceptibility of a sequence of amorphous Fe-Mn alloys shows lines of both spin-glass and ferromagnetic transitions. A detailed scaling-law analysis, treating the common point on the two magnetic phase boundaries as a multicritical point, verifies the scaling hypothesis and yields multicritical, spin-glass, and crossover exponents. The observed behavior compares quite will with position-space renormalization results.

It is now generally accepted that materials with competing exchange interactions may become spin-glasses at low temperatures, rather than acquiring long-range order in the usual sense.[1-3] There is far from general agreement, however, as to whether the spin-glass state is achieved through a phase transition or a more gradual freezing process. In this Letter, we report the results of a detailed study of the transition from a ferromagnet to a spin-glass as a function of material composition. We show, for the first time, that the magnetic susceptibility along both the spin-glass and ferromagnetic lines satisfies a scaling hypothesis appropriate to a multicritical point common to both lines. This strongly implies that there is a competition between the length scales for ferromagnetic and spin-glass order, with both simultaneously divergent at the special point, which we will refer to as "bicritical." In the course of the analysis, the critical, bicritical, and crossover exponents are also determined. We assert that the applicability of scaling laws along the spin-glass line indicates that this is a line of phase transitions.

The materials chosen for this study are well-characterized amorphous alloys with the composition $(Fe_{1-x}Mn_x)_{75}P_{16}B_6Al_3$.[4,5] Alloys were prepared with $0 \leq x \leq 1$ by centrifugal spin quenching.[6] We report here results for alloys in the range $0.3 \leq x \leq 0.6$, in steps of 0.05. There are several reasons for this choice of material:

(i) The alloys can be prepared in a single phase for all values of x.[6]

(ii) Rapid quenching preserves the liquid state of the melt, thus avoiding possible chemical clustering effects.

(iii) Crystal-field, magnetocrystalline-anisotropy, and grain-boundary effects are minimized in these amorphous materials.

(iv) Fe and Mn atoms have local moments with nearly equal spin, so that the material approximates a bond-random model for the ferromagnet–spin-glass phase diagram.

Ribbons of the amorphous alloys were cut to approximately 3 mm× 1 mm× 25 μm and packed in the coil of an ac susceptibility bridge, with the longer dimension along the coil axis. The ac susceptibility was measured in a field of ≈ 3 Oe (rms) at 400 Hz, but a check at several frequencies between 100 Hz and 1 kHz showed no significant differences. Data taken both during warming and cooling were completely reproducible. The susceptibility at larger values of x shows the characteristic spin-glass cusp as may be seen in Fig. 1. As x is reduced, the peak temperature increases, as does the peak amplitude. At $x = 0.4$, the ac susceptibility signal becomes equal to the inverse of the demagnetizing factor N. For smaller x, the ac susceptibility shows a flattened top, indicating that the susceptibility is much larger than N^{-1}. To proceed with an analysis of the susceptibility, we first calculate the actual suscepti-

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