Two FeH pairs in *n*-type Si and their implications: A theoretical study

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Experimental evidence for interstitial {FeH} pairs in *n*-type Si stems from thermally stimulated capacitance (TSCAP). Electron-paramagnetic resonance (EPR) data have also been interpreted in terms of {FeH} pairs. We present theoretical studies of two {FeH} pairs. The properties of the first match those of the TSCAP center but are incompatible with the EPR center. The second is a possible candidate for the EPR center. If true, this suggests that high-temperature anneals can introduce substitutional Fe in concentrations higher than commonly believed.

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Transition metal (TM) impurities such as Fe are common and undesirable contaminants in both integrated-circuit and photovoltaic Si materials. Istratov *et al.*[1,2] have reviewed the properties of Fe in Si.

Several authors have hydrogenated samples containing TM impurities in an effort to passivate[3] them or at least reduce their electrical activity. In the 3*d* series, the consequences of hydrogenation by remote plasma, wet chemical etching, or H implantation have been reported for Ti,[4,5] V,[4,6,7] Cr,[4,6] Fe,[8–14] Co,[15] Ni,[16] and Cu.[17–20] Following hydrogenation, the electrical levels of the TM impurity have been monitored by deep-level transient spectroscopy (DLTS), Laplace DLTS, or thermally stimulated capacitance (TSCAP). In some cases, deep-level depth profiling was used[19,20] to determine how many H's are trapped at a given TM. The $\{TM,H_n\}$ complexes with $n=1$, 2, and 3 remain electrically active, but the levels shift within the gap.

Tavendale and Pearton[8,9] exposed Fe-contaminated samples to a H plasma. They found no Fe-related DLTS lines in *n*-type Si and reported that the donor level of Fe_i is not affected by H in *p*-type Si. However, both Fe_i and H are in the + charge state in this material.

Kouketsu *et al.*[10] studied the gap levels of interstitial iron (Fe_i) and the iron-boron pair ($\{Fe_iB_s\}$) following H^+ implantation. They found that their donor levels are reduced and assigned it to H passivation. But vacancies, generated by the implantation, are predicted[21] to interact with Fe_i and $\{Fe_iB_s\}$, forming Fe_s and $\{Fe_sB_s\}$, respectively. These defects have no donor level in the gap. Theory also predicts[22,23] that $\{Fe_iH\}$ has both donor ($E_v+0.36$ eV) and acceptor ($E_c-0.26$ eV) levels, and that H does not bind to the $\{Fe_iB_s\}$ pair (the stable configuration has isolated Fe_i and a {HB} pair).

Sadoh *et al.*[12] diffused Fe (2 h at 930 °C) into P-doped Si samples (10^{14} cm^{-3}), introduced H by chemical etching, and performed TSCAP experiments with minority-carrier injection. They observed isolated Fe_i (donor level at $E_v+0.41$ eV) and a donor level at $E_v+0.31$ eV, which they assigned to $\{Fe_iH\}$. It anneals out in 30 min at 175 °C. Since Fe_i is in the zero-charge state in *n*-type Si and H probably diffuses as neutral bond centered H^0_{BC}, they proposed the reaction $Fe_i^0+H_{BC}^0\rightarrow\{Fe_iH\}^0$.

Takahashi *et al.*[13,14] diffused ^{57}Fe at 950–1250 °C into P-doped ($\sim10^{16}$ cm^{-3}) Si with, as well as without, H_2 in the ampoule. During this treatment, H_2 breaks up at the Si surface and H diffuses in atomic form into the bulk.[24,25] The samples were quenched to 10 K and electron-paramagnetic resonance (EPR) experiments were performed. Distinct isotropic spectra are observed with and without H_2 in the ambient. The EPR data lack detail and their interpretation is not unique.

Figure 1 in Refs. 13 and 14 suggests that the EPR spectrum without H ("spectrum I") corresponds to a defect with electronic spin 1/2, 1, or 3/2 in T_d symmetry. The resonant frequency of 9.1 GHz at 313 mT gives a *g* value of 2.07. The line splitting of 0.8 mT leads to a hyperfine splitting constant of $\sim7.7\times10^{-4}$ cm^{-1}. These numbers are close to those obtained[26] for Fe_i: 2.07 and 7.0×10^{-4} cm^{-1}, respectively. Thus, in *n*-Si, spectrum I could be neutral Fe_i (spin 1). It could also be substitutional iron (Fe_s) in the zero-charge state (spin 1/2). The latter has not been detected by EPR.

A different EPR line appears when H_2 and ^{57}Fe are both in the ambient during the high-*T* in-diffusion. This signal is isotropic, implying a defect with T_d symmetry on the average. The positions of two maxima and two minima of the EPR line precisely match the maxima and minima of spectrum I, strongly suggesting that the line is not a single spectrum but the sum of two spectra, one of which is spectrum I with intensity reduced by about 2/3 of that without H in the sample. Removing this 2/3 of spectrum I from the line produces "spectrum II," which has no hyperfine splitting and could correspond to a defect with electronic spin 1/2, 1, or 3/2. The line anneals out around 225 °C.

It has been suggested[27] that the presence of H_2 in the ampoule could result in ^{56}Fe contamination from the quartz walls of the ampoule and that the EPR line is a superposition of $^{56}Fe_i$ and $^{57}Fe_i$. However, the $^{57}Fe_i$ line (spectrum I) should remain dominant instead of dropping by 2/3 in intensity. Further, the annealing rates of spectrum I and the EPR line are distinct (Fig. 4 in Ref. 13), suggesting distinct defects. The authors[13,14] propose that a {FeH} pair forms and that H tunnels (or hops very fast) around Fe.

We denote the spin/charge state of a defect X as $^{spin}X^{charge}$. The EPR spectra I and II could be $^{1}Fe_i^0$ and $^{1/2}\{Fe_iH\}^0$, respectively; or the isotopes 56 and 57 of $^{1}Fe_i^0$, respectively; or $^{1/2}Fe_s^-$ and $^{1/2}\{Fe_sH\}^0$ (see below), respectively. However, the EPR spectra are isotropic. We will show (below) that this rules out the first option as $^{1/2}\{Fe_iH\}^0$ is always trigonal. Although accidental contamination can

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never be ruled out, we examine here the properties of the $\{Fe_sH\}$ pair.

Fe_s has been seen in Mn-implanted Si by Mössbauer spectroscopy[28–31] and by channeling.[32] However, Fe_i is assumed to be the only form of isolated iron in Si when Fe is in-diffused at high temperatures.[1] But is this always true? Fe_s is predicted[21] to have no donor but a deep acceptor level at $E_c-0.41$ eV instead. Kaminski *et al.*[33] tentatively assigned the trap P11 (380 meV) to an acceptor state of Fe_s. Theory also predicts[21] that Fe_s has low spin, ${}^{0}Fe_s^0$ in *p*-type Si and ${}^{1/2}Fe_s^-$ in *n*-type Si.

We present here the results of theoretical studies of H interactions with Fe_i and Fe_s using the methods described and tested in Refs. 21–23. In order to double-check the predictions, the calculations were carried out using both VASP (Ref. 34) and SIESTA (Ref. 35) within the generalized gradient approximation.[36,37] The two sets of results are systematically close to each other.

The plane-wave VASP calculations use projector augmented-wave potentials[38] with a cutoff of 398 eV. The SIESTA calculations use norm-conserving pseudopotentials in the Troullier-Martins form.[39] The Fe pseudopotential has been optimized by Izquierdo *et al.*[40,41] It includes nonlinear core corrections. Pruneda *et al.*[42] have studied Fe/Si systems and shown that the pseudopotential/SIESTA approach provides results in excellent agreement with the all-electron tight-binding linear muffin-tin orbital method.

The SIESTA basis sets for the valence states are linear combinations of numerical atomic orbitals.[35,43] We use double-zeta (DZ) basis sets (two sets of *s* and *p*'s) for H and polarized basis sets (DZ plus one set of *d*'s) for Si and Fe. The charge density is projected on a real-space grid with an equivalent cutoff of 250 Ry to calculate the exchange-correlation and Hartree potentials.

The host crystal is represented by a 64 host atoms periodic supercell. The lattice constant is optimized in each charge state. A $3\times3\times3$ Monkhorst-Pack[44] mesh is used to sample the Brillouin zone. The geometries are optimized with a conjugate gradient algorithm.

The gap levels are estimated using the marker method.[45] The calculated ionization energies and electron affinities are scaled to a marker (we use the perfect crystal). The same scaling is used to obtain the donor and acceptor levels of the defect. We have calculated numerous Fe-related donor and acceptor levels[21,23] with an average accuracy better than 0.1 eV.

The transition states are calculated using the climbing-image nudged-elastic-band method[46] implemented in the plane-wave-based QUANTUM-ESPRESSO package.[47] For these calculations, a kinetic-energy cutoff of 35 Ry is used and the Γ point for *k*-point sampling. The electron-ion interaction is described by ultrasoft Vanderbilt pseudopotentials.[48]

The $\{Fe_iH\}$ pair has been reported earlier.[22,23] Fe_i is at the tetrahedral interstitial (*T*) site. When it traps H, Fe_i moves to the hexagonal interstitial site and H points toward the *T* site along the trigonal axis with Fe-H=1.51 Å (Fig. 1, Ref. 23). This pair does not form in *p*-type material where both Fe and H are positively charged. In intrinsic and *n*-type Si, Fe_i is in the zero-charge state and H can diffuse as H_{BC}^0 or, more slowly, as H_T^-. Using the reaction proposed by Sadoh *et al.*,[12] the binding energy is

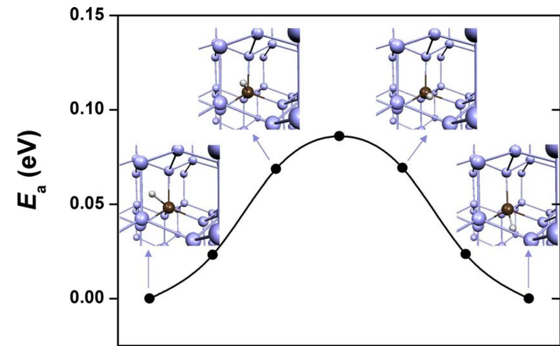
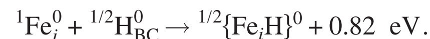


FIG. 1. (Color online) Activation energy for rotation E_a (eV) of H around Fe_s. The classical barrier is 0.08 eV. The insets show intermediate positions of H (white circle) as it rotates around Fe_s (black circle). A few of the neighboring Si atoms are shown in blue (gray).



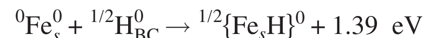
$$ {}^{1}Fe_i^0 + {}^{1/2}H_{BC}^0 \rightarrow {}^{1/2}\{Fe_iH\}^0 + 0.82\ \text{eV}. $$

The $\{Fe_iH\}$ pair has both a donor level at $E_v+0.36$ eV and an acceptor level at $E_c-0.26$ eV. In the + and − charge states, the lowest-energy spin state is 1 and the binding energy is smaller (∼0.4 eV).

The properties of $\{Fe_iH\}$ agree with the defect described by Sadoh *et al.*[12] It appears following hydrogenation, the calculated donor level ($E_v+0.36$ eV) is close to the measured one ($E_v+0.31$ eV) and the binding energy (0.82 eV) is consistent with the low annealing temperature (175 °C). $\{Fe_iH\}$ is always trigonal. H cannot squeeze through the hexagonal site with Fe already there. The only possible reorientation from one trigonal axis to another involves the dissociation of the pair. Even if H could somehow tunnel around Fe_i, the defect would have trigonal, not tetrahedral, symmetry.

The {FeH} pair assigned to the EPR spectrum II is isotropic. Takahashi *et al.*[13,14] suggested that H is tunneling around Fe, or at least rotating fast enough at $T=10$ K, to be isotropic in the EPR experiments. Further, the annealing temperature of the EPR spectrum is higher than that of $\{Fe_iH\}$.

The calculated properties of the $\{Fe_sH\}$ pair in the zero-charge state are consistent with the EPR center. Hydrogen binds directly to Fe_s without perturbing any of the four Fe_s-Si bonds (this is similar[20] to $\{Cu_sH\}$). The calculated binding energy in the EPR-active state



$$ {}^{0}Fe_s^0 + {}^{1/2}H_{BC}^0 \rightarrow {}^{1/2}\{Fe_sH\}^0 + 1.39\ \text{eV} $$

is larger than that of ${}^{1}\{Fe_iH\}^0$ (0.82 eV). Both values are consistent with the reported annealing temperatures of these defects, 225 and 175 °C, respectively.

The $\{Fe_sH\}$ pair has no donor level but an acceptor level at $E_c-0.62$ eV. The lowest-energy states are ${}^{1/2}\{Fe_sH\}^0$ (Fe_s-H along ⟨100⟩) and ${}^{0}\{Fe_sH\}^-$ (Fe_s-H along ⟨111⟩). The ${}^{1}\{Fe_sH\}^-$ state is 0.23 eV higher in energy. Since Fe_s exists as ${}^{0}Fe_s^0$ or ${}^{1/2}Fe_s^-$, only the −1 charge state of Fe_s and the zero-charge state of $\{Fe_sH\}$ are EPR active, both with spin 1/2.

$\{Fe_sH\}$ has tetrahedral symmetry on the average. The potential-energy surface for H rotating around Fe_s is extremely flat (Fig. 1). The classical barrier for rotation is 0.08

eV. The quantum value is smaller since, at the saddle point, the wag mode contributions to the zero-point energy are missing. They are of the order of 0.08 eV.

Since our methodology treats nuclei classically, we cannot comment on the issue of H tunneling around Fe_s. However, the classical height is small enough for H to rotate around Fe_s on a very short-time scale. Indeed, molecular-dynamics simulations show that H rotates around Fe_s in about 70 fs at 500 K.

Note that this time scale for rotation is comparable to period of the Fe_s-H stretch vibration, predicted[22] to be at 1663 cm^{-1}. This value was calculated with H in its lowest-energy position. But since H moves around Fe_s about as fast as it undergoes one oscillation, it experiences an average potential. This makes it impossible to predict a precise value for the Fe_s-H stretch frequency. No wag mode is expected.

As is the case for TMs such as Cu_s (Ref. 20) or Pt_s,[49] Fe_s can trap more than one H, although high concentrations of complexes such as $\{Fe_sH_n\}$ with $n>2$ are unlikely. We find that ${}^{1/2}\{Fe_sH\}^0 + {}^{1/2}H^0_{BC} \rightarrow {}^0\{HFe_sH\}^0 + 1.75$ eV. The two H atoms rotate around Fe_s with an activation energy of 022 eV. This complex has an acceptor level at $E_c - 0.71$ eV.

The key points of this Brief Report are as follows: (1) First-principles theory predicts two Fe-H pairs in Si. $\{Fe_iH\}$ has Fe_i at the hexagonal interstitial site and is always trigonal. It has a donor ($E_v + 0.36$ eV) and an acceptor ($E_c - 0.26$ eV) levels in the gap and a binding energy of about 0.8 eV in the zero-charge state. $\{Fe_sH\}$ has H rotating around Fe extremely fast leading to a defect that averages out to tetrahedral symmetry. It has no donor but an acceptor ($E_c - 0.62$ eV) level in the gap. The binding energy is ~ 1.4 eV in the zero-charge state. (2) The precursor, gap level, and binding energy of $\{Fe_iH\}$ are consistent with the Fe-H pair reported in the TSCAP measurements following H introduction by wet chemical etching. However, this pair cannot give rise to an isotropic EPR center. The symmetry and binding energy of $\{Fe_sH\}$ are consistent with the properties of the isotropic EPR center seen following exposure to H at high temperatures. $\{Fe_sH\}$ has no donor level in the gap. (3) Theory cannot rule out that the EPR data have been misinterpreted and that contamination is to blame for spectrum II. However, if we assume that the isotropic EPR center is indeed associated with a {FeH} pair, then Fe_s must form during the high-temperature in-diffusion of Fe into *n*-type Si, in concentrations high enough to be seen by EPR ($\sim 10^{16}$ cm^{-3}).

In *p*-type Si, Fe_s can easily escape detection since it has spin 0 and no donor level. Theory predicts that it has an acceptor level at $E_c - 0.41$ eV, a value close to the P11 trap[33] at $E_c - 0.38$ eV. In *n*-type Si, Fe_s has spin 1/2 and therefore could give rise to the EPR spectrum I discussed above.

When Fe_i encounters a pre-existing vacancy, it forms Fe_s with a gain in energy[21] of 2.92 eV (at $T=0$ K). In P-doped Si, our calculations show that the energy gain is ~ 0.2 eV larger when Fe_s is near P. The formation enthalpy[50] of the vacancy in Si is 3.6 eV. Thus, at low temperatures, Fe_i does not become Fe_s. The vacancy must be provided (implantation, plasma exposure, etc.). However, at the in-diffusion temperature, a large (mostly configurational) entropy contribution[51] tilts the free-energy balance in favor of the formation of Fe_s. The presence of H in the material at high temperatures may also affect the free-energy balance.

Calculating the enthalpies involved in such processes is far beyond the scope of this Brief Report. However, a second look at some samples might be warranted, with an eye on the predicted acceptor level of Fe_s. More detailed EPR studies of the consequences of Fe or $Fe + H_2$ in-diffusion into *n*-type Si would also be of interest.

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