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# Evaluation of Structurally Metastable Iron-Boron Pairs in Silicon

H. NAKASHIMA, T. SADOH, and T. TSURUSHIMA

*Department of Electrical Engineering, Kyushu University, Fukuoka 812, JAPAN*

Structurally metastable $Fe_i$-$B_s$ pairs in Si have been for the first time detected by using dark or photo capacitance-transient technique combined with minority-carrier injection below 200 K. Five levels at $E_C - 0.43$ eV, 0.46 eV, 0.52 eV, and 0.54 eV and $E_V + 0.53$ eV are observed as the metastable defects. The annihilation behaviors have been investigated by isochronal and isothermal anneals. From these investigation, the pair configurations responsible for these defect levels are proposed.

## 1. INTRODUCTION

Iron is a principal contaminant during Si device fabrication. Because of its high diffusion coefficient, Fe ions are unstable at room temperature and tend to form complexes with other impurities. In B-doped p-type Si, the mobile interstitial $Fe_i^+$ is captured by substitutional $B_s^-$, forming $Fe_i$-$B_s$ pair which has the structure of $Fe_i$ on the 1st nearest tetrahedral ($T_d$) site adjacent to $B_s$.[1)] It is well established[2-4)] that the level at $E_V + 0.1$ eV is due to a donor ($Fe_i^{+/++}B_s^-$) of the 1st nearest $Fe_i$-$B_s$ pair and that at $E_V + 0.4$ eV is due to a donor ($Fe_i^{0/+}$) of the isolated $Fe_i$.

According to the ion pairing theory,[3)] the pair formation causes pushing of $Fe_i$ donor level towards the conduction band, and thus the 1st nearest $Fe_i$-$B_s$ pair should have an acceptor level ($Fe_i^{0/+}B_s^-$). Recently, we have confirmed using the photo capacitance technique that the level at $E_C - 0.29$ eV is due to the 1st nearest site $Fe_i$-$B_s$ pairs.[5)] In addition, Gehlhoff and Rehse have found a negative charge state of the trigonal $Fe_i$-$B_s$ pairs by using photo electron paramagnetic resonance (EPR), which cause an acceptor level at $E_C - (0.25 \pm 0.05)$ eV.[6)] From these new results, it is clear that the acceptor level around $E_C - 0.29$ eV is due to the 1st site $Fe_i$-$B_s$ pairs.

The pairs dissociate even below room temperature by minority-carrier injection from $n^+p$ junction.[3)] This implies that $Fe_i$ ions jump from the 1st nearest site to another by obtaining the recombination energy. If low-level injection is carried out at such a low temperature that $Fe_i$ cannot thermally migrate, it should be possible that $Fe_i^+$ ions remain at structurally metastable sites bounded to $B_s^-$. Thus, it is expected that energy levels for the metastable sites emerge between the acceptor level of the stable 1st nearest site $Fe_i$-$B_s$ and the donor level of the isolated $Fe_i$. However, the metastable defects have not yet been confirmed experimentally. We have for the first time succeeded in detecting the metastable $Fe_i$-$B_s$ pairs.[5,7)] In this paper, we present on the annihilation behaviors of the metastable $Fe_i$-$B_s$ pairs in Si by using dark or photo capacitance methods combined with minority-carrier injection below 200 K.

## 2. EXPERIMENTAL

We employed a mesa-type Fe-doped $n^+p$ junction sample (B content: $1.0 \times 10^{14}$ cm$^{-3}$; Fe content: $3 \times 10^{13}$ cm$^{-3}$). The sample size is $3.5 \times 3.5 \times 0.5$ mm$^3$. A cylindrical cavity with diameter 2 mm was made from the back surface to the front. The effective sample thickness was about 0.1 mm.

The technique for detecting minority-carrier trap is as follows: The back surface of the $n^+p$ diode reverse-biased at $V_R$=10 V was illuminated with He-Ne laser light (power: 10 mW; wavelength: 0.63 $\mu$m; absorption depth: 3 $\mu$m), which was led to the cavity of the sample by an optical fiber. This procedure enabled us to introduce only minority carriers in the depletion region. When the optical source was switched off, electron emission from minority-carrier trap occurred at appropriate temperature, and thus the emission process could be observed by recording the capacitance change after the illumination. Majority-carrier trap was observed by recording the capacitance change with $V_R$=10 V after applying zero bias in darkness. The capacitance technique used were deep level transient spectroscopy (DLTS), thermally stimulated capacitance (TSCAP), and single shot. Minority-carrier injection was accomplished using a constant current source in series with the diode.

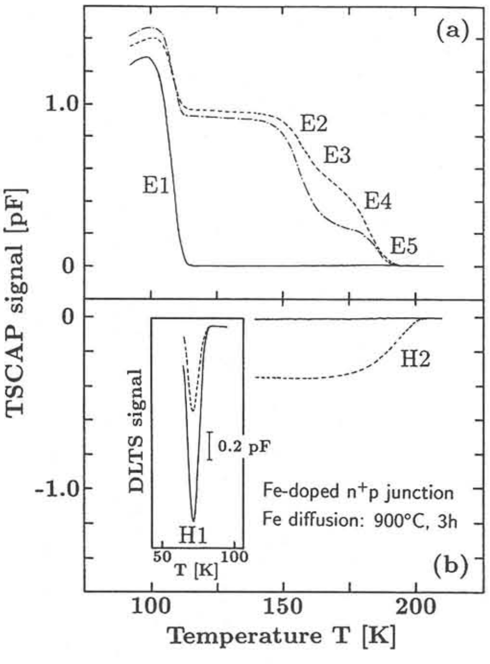


Fig. 1. TSCAP signals for (a) electron- and (b) hole-trapping levels for Fe-doped p-type Si. The inset shows DLTS signals. Solid line: before injection; broken line: after the injection of $J_F$ =10 mA/cm$^2$ for 200 s; dash-dotted line: after annealing at 210 K for 10 min following the injection. The TSCAP signal represents the capacitance difference between upward scan data and downward data. The TSCAP results (a) and (b) were obtained after illuminating 0.63 $\mu$m light at 80 K and applying the zero bias at 130 K, respectively. The DLTS signals were generated under a gate setting $t_1/t_2 = 0.02/0.2$ ms.

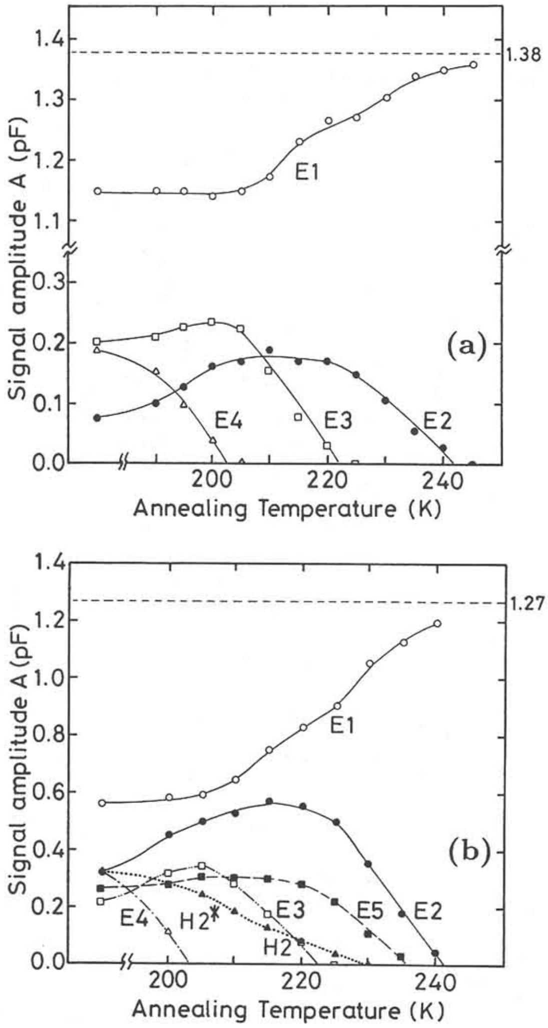


Fig. 2. Isochronal anneals data for metastable Fe$_i$-B$_s$ pairs. The anneals were performed for 10 min under the zero bias condition. (a): after the injection of $J_F$ =10 mA/cm$^2$ for 10 s at 150 K; (b): after the injection of $J_F$ =10 mA/cm$^2$ for 200 s at 150 K; ○:level E1; ●: E2; □: E3; △: E4; ■: E5; ▲: H2.

## 3. RESULTS AND DISCUSSION

Typical TSCAP and DLTS results before and after injection at 150 K are shown in Figs. 1(a) and 1(b), where electron- and hole-trapping levels are labeled '$E$' and '$H$', respectively. Only two levels $E1$ at $E_C - 0.29$ eV and $H1$ at $E_V + 0.10$ eV are observed before the injection. The levels are due to an amphoteric center of the 1st nearest Fe$_i$-B$_s$ pairs.[7] By contrast, the injection leads to strong decrease of $E1$ and $H1$ and to emergence of four electron-trapping levels $E2$-$E5$ and a hole-trapping level $H2$. The level E4 annihilates after annealing at 210 K, as shown by the dash-dotted line in Fig. 1(a). The level positions determined from single shot measurements are as follows: [5,7] $E2$: $E_C - 0.43$ eV; $E3$: 0.46 eV; $E4$: 0.52 eV; $E5$: 0.54 eV; $H2$: $E_V + 0.53$ eV.

Figures 2(a) and 2(b) show the results obtained from the isochronal anneals for 10 min at zero bias. For the case of weak injection (Fig. 2(a)), levels $E2$, $E3$, and $E4$ are created. The level $E4$ vanishes at low temperature of 205 K. Its annihilation leads to the increase of $E2$ and $E3$ but does not lead to the increase of $E1$, suggesting that the thermal return path is $E4 \rightarrow E2$ and $E3$. The level $E3$ annihilates at around 220 K. Since its annihilation causes the increase of $E1$, the path is $E3 \rightarrow E1$. The level $E2$ shows the stable behaviors vanishing at around 240 K, and the path is clearly $E2 \rightarrow E1$.

For the case of moderate injection (Fig. 2(b)), levels $E5$ and $H2$ are also observed. The level $E5$, as well as $E2$, is thermally stable defect. Though the path for $E5$ is ambiguous from the isochronal data, the isothermal anneal results at 230 K after the same injection reveal that the return path is $E5 \rightarrow E1$. All these levels $E2$-$E5$ rapidly disappear within 15~ 20 K from the onset of the annihilation. By contrast, the disappearance of level $H2$ proceeds slowly in the wide temperature range 200-230 K, indicating that the level $H2$ consists of two components due to trap $H2^*$ vanishing at around 215 K and trap H2 vanishing at 230 K. The annihilation of traps $H2^*$ and $H2$ lead to the increase of trap $E2$, indicating that these traps return to $E2$, i.e., probably $H2 \rightarrow H2^* \rightarrow E2$.

In order to investigate jumping process of Fe$_i^+$ on each structurally metastable site, isothermal anneals under

TABLE I. Annihilation temperature $T_{an}$, thermal return path, diffusion barrier height $E_D$, and level positions $E_P^{exp}$ obtained from the experiment and $E_P^{cal}$ from the calculation for metastable $Fe_i$-$B_s$ pairs.

| trap | path | $T_{an}$ [K] | $E_D$ [eV] | $E_P^{exp}$ [eV] | $E_P^{cal}$ [eV] | site |
|---|---|---|---|---|---|---|
| $E1$ | | — | — | $E_C - 0.29$ | — | 1st $T_d$ |
| $E2$ | $\longrightarrow E1$ | 242 | 0.75 | $E_C - 0.43$ | $E_C - 0.36$ | 2nd $T_d$ |
| $E3$ | $\longrightarrow E1$ | 223 | — | $E_C - 0.46$ | — | ? |
| $E4$ | $\longrightarrow E2, E3$ | 204 | — | $E_C - 0.52$ | — | ? |
| $E5$ | $\longrightarrow E1$ | 238 | 0.73 | $E_C - 0.54$ | $E_C - 0.55$ | 4th $T_d$ |
| $H2^*$ | $\longrightarrow E2$ | 215 | — | $E_V + 0.53$ | — | ? |
| $H2$ | $\longrightarrow E2$ | 230 | 0.68 | $E_V + 0.53$ | $E_V + 0.56$ | 3rd $T_d$ |

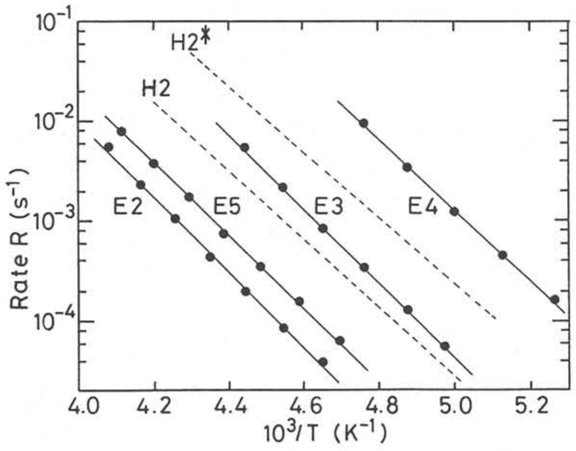


Fig. 3. Decay rates $R$ of traps $E2$, $E3$, $E4$, and $E5$ as a function of reciprocal temperature. The broken lines represent $R$ of traps $H2$ and $H2^*$.[7)]

zero bias were carried out. The decay rates $R$ for traps $E2$-$H2$ obtained are plotted in Fig. 3 as a function of temperature $T$; they can be fitted by the following expressions:

$$R_{E2} = 1.3 \times 10^{13} \exp(-0.75 \text{ eV}/kT) \text{ s}^{-1}, \quad (1)$$
$$R_{E3} = 1.9 \times 10^{14} \exp(-0.74 \text{ eV}/kT) \text{ s}^{-1}, \quad (2)$$
$$R_{E4} = 5.6 \times 10^{14} \exp(-0.70 \text{ eV}/kT) \text{ s}^{-1}, \quad (3)$$
$$R_{E5} = 1.1 \times 10^{13} \exp(-0.73 \text{ eV}/kT) \text{ s}^{-1}, \quad (4)$$
$$R_{H2^*} = 6.0 \times 10^{12} \exp(-0.65 \text{ eV}/kT) \text{ s}^{-1}, \quad (5)$$
$$R_{H2} = 3.9 \times 10^{12} \exp(-0.68 \text{ eV}/kT) \text{ s}^{-1}. \quad (6)$$

The rates except for $R_{E3}$ and $R_{E4}$ seem to originate from the barrier to atomic motion of $Fe_i^+$ ion from one configuration to another because the preexponential factors are indeed in the range $10^{12} - 10^{13}$ s$^{-1}$ expected from a single jump process. The thermal activation energies $E_D$ obtained are rather larger than that (0.66 eV)[8)] of free $Fe_i^+$ determined in the range 273-1343 K. This might be related to the lattice strain in the vicinity of $B_s$.

We discuss the positions of $Fe_i^+$ in the vicinity of $B_s^-$. Most stable sites should be $T_d$ interstitial sites because of large metallic radius of $Fe_i$. Thus, we suggest that thermally stable traps $E2$, $E5$, and $H2$ are attributed to $T_d$ sites in the vicinity of $B_s^-$. The level positions $E_P^{cal}$ of $Fe_i^+$ at the $T_d$ sites are calculated using the configuration coordinate description[5,7,9)] based on the simple ionic model. The experimental and calculated results are summarized in Table I. Among the $T_d$ sites in the vicinity of $B_s^-$, $Fe_i^+$ on the 2nd and 4th sites are back to the 1st site by a single jump, while $Fe_i^+$ on the 3rd site returns to the 2nd site. From this consideration and the correspondence of the level position $E_P^{cal}$ to $E_P^{exp}$, traps $E2$, $H2$, and $E5$ can be assigned to the 2nd, 3rd and 4th sites, respectively. Since the annihilation of the traps $E3$, $E4$, and $H2^*$ are fast, these traps seem to be attributed to unstable positions such as the hexagonal site or quite different sites due to lattice strain in the vicinity of $B_s^-$.

## 4. SUMMARY

We have studied the structurally metastable $Fe_i$-$B_s$ pairs in Si by using dark or photo TSCAP and single shot techniques combined with minority-carrier injection. From the investigation of isochronal and isothermal anneals for the metastable defects, electrical and thermal properties of the metastable defects have been characterized. It is proposed that levels at $E_C - 0.43$ eV, $E_V + 0.53$ eV and $E_C - 0.54$ eV are originated from $Fe_i^{+/0}$ of the 2nd, 3rd, and 4th nearest $T_d$ sites adjacent to $B_s^-$, respectively.

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