

Ultrasound stimulated dissociation of Fe-B pairs in silicon

S. S. Ostapenko^{a)} and R. E. Bell

Center for Microelectronics Research, University of South Florida, Tampa, Florida 33620

(Received 26 October 1994; accepted for publication 26 January 1995)

We found that application of ultrasound vibrations to *p*-type silicon promotes a dissociation of iron-boron pairs. This effect is manifested by a decrease of the minority carrier diffusion length, L , after ultrasound treatment (UST) of the silicon wafer. Post-UST recovery of the diffusion length is identical after thermal and optical pair dissociation. This provides an unambiguous proof for dissociation of Fe-B pairs stimulated by ultrasound vibrations. The UST process creates interstitial iron donors which acts as efficient recombination centers and lower the L value. A relevant physical mechanism of the ultrasound effect is discussed. © 1995 American Institute of Physics.

In the early 1980's,¹ it was observed that ultrasound treatment, UST, of semiconductor crystals had a profound effect on recombination properties. It was suggested that the vacancy-self-interstitial generation and/or dissociation of complex centers stimulated by ultrasound vibrations are responsible for a dramatic change of luminescence spectra in II-VI.^{1,2} It was recently observed that UST changes the minority carrier diffusion length in Czochralski silicon wafers³ and solar-grade polycrystalline silicon.⁴ The process of Fe-B pair dissociation enhanced by ultrasound vibrations, was suggested as a relevant mechanism. Present work provides positive proof for this mechanism which, on the other hand may be key to an understanding of low-temperature Fe gettering stimulated by ultrasound vibration in solar-grade silicon.⁴

In *p*-type silicon, the positively charged interstitial donor, Fe^+ , mobile at room temperature ($D=10^{-15} \text{ cm}^2/\text{s}$) and forms nearest-neighbor pairs with substitutional acceptor, e.g., boron.⁵ Both states of iron, i.e., the pair and isolated interstitial, give energy levels in the silicon energy gap. The energy of a neutral pair, $(\text{FeB})^0$, is located at $E_v+0.1 \text{ eV}$, while a deep donor level $E_v+0.4 \text{ eV}$ is attributed to an isolated Fe_i (Ref. 6). A "fingerprint" of Fe-B pairs is a specific low-temperature pairing kinetics observed after thermal pair dissociation (annealing at about 200°C)⁷ or after recombination enhanced dissociation caused by injection of minority carriers under light illumination⁸ or junction current.⁶ For iron concentrations, $[\text{Fe}]$, small as compared to the boron concentration, $[\text{B}]$, the pairing kinetics follow the first order reaction for $T=290\text{--}350 \text{ K}$ and $[\text{B}]=10^{14}\text{--}10^{16} \text{ cm}^{-3}$. The pairing time constant, τ_p , is given by^{5,7}

$$\tau_p(\text{min}) = (7.17 \times 10^3)(T) \exp(0.68/kT)/[\text{B}](\text{cm}^{-3}). \quad (1)$$

The dissociation-association reaction, $(\text{FeB}) \leftrightarrow \text{Fe}_i + \text{B}_s$, can be monitored by a change of minority carrier diffusion length, L , caused by a large difference (by a factor of about 10) in the electron capture cross section between the pair and the interstitial iron. As discussed in Ref. 7, the breaking of

the pairs is accompanied by a decrease of the diffusion length value from L_0 to L_1 . They are quantitatively related to the concentration of pairs, N_{FeB} , as follows:

$$N_{\text{FeB}}(\text{cm}^{-3}) = 1.06 \times 10^{16} (L_1^{-2} - L_0^{-2})(\mu\text{m}^{-2}). \quad (2)$$

In this study, the diffusion length before (L_0) and after pair dissociation (L_1) was measured using the surface photovoltage (SPV) method.^{7,9}

The samples used in our study were boron-doped Cz-silicon wafers with $[\text{B}]=5 \times 10^{14} \text{ cm}^{-3}$. This relatively low boron concentration resulted in a low thermal pairing rate thereby providing a favorable condition for studying the effects of UST. The $[\text{Fe}]$ concentration was 0.8 to $1.5 \times 10^{14} \text{ cm}^{-3}$ was determined using SPV and optical pair dissociation technique.⁸ By comparing optical and thermal pair dissociation, it was established that the concentration of chromium was negligible in comparison to that of iron. For the UST experiments, a circular external piezoelectric transducer with a resonant frequency in the range of $25\text{--}70 \text{ kHz}$ was bound to the back surface of a wafer. Radial ultrasound vibrations were generated into crystal with an acoustic strain amplitude of $10^{-5}\text{--}10^{-4}$ measured by a miniature acoustic wave detector. The transducer and sample were placed on a temperature-controlled chuck. The temperature of the sample, during UST and post-UST relaxation, was controlled *in situ* with both an infrared pyrometer and a thermocouple attached to the sample surface. A computer controlled commercial SPV system was used for a noncontact measurement of minority carrier diffusion length. Details of the SPV technique are described in Ref. 9.

The kinetic cycle of isothermal UST of diffusion length (ultrasound is on) followed by post-UST relaxation of L (ultrasound is off) is shown in Fig. 1. Prior to treatment, the sample was kept at room temperature. The sample and transducer were then placed on a heated chuck and the UST started at 75°C at $t=0$. After the treatment, the sample was rapidly cooled to room temperature by placing it on an aluminum plate and the L value was measured with the SPV technique. The same steps were performed with increasing treatment times to provide a kinetic curve of UST. The results are shown by the filled squares in Fig. 1. They demonstrate a strong decrease of the diffusion length due to the UST. The recovery of the diffusion length is shown in Fig. 1 with the empty squares. We would like to emphasize that the

^{a)}On leave from Institute of Semiconductor Physics, Academy of Sciences, pr Nauki 45, Kiev 252028, Ukraine; Electronic mail: ostapenk@felix.cmd.usf.edu

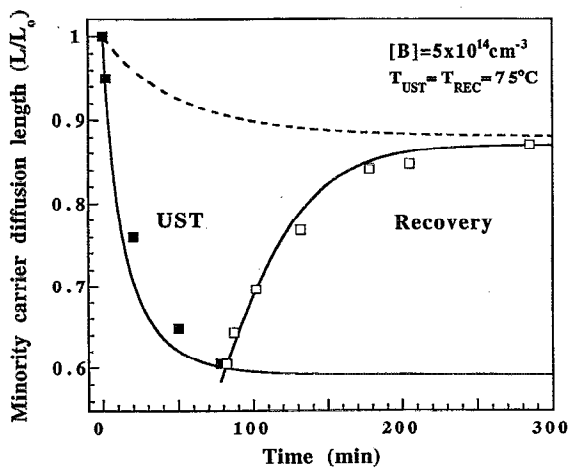


FIG. 1. Isothermal kinetics of the ultrasound treatment of the minority carrier diffusion length (filled points) and post-UST relaxation (empty points) at 75 °C. The solid lines represent a theoretical fit of the pair dissociation and association using solution of Eq. (3) with parameters: $\tau_p=32$ min; $\tau_{UST}=134$ min; and $\tau_p=960$ min. Dotted lines show the kinetics of thermal dissociation at 75 °C.

same temperature ($T=75$ °C) was also maintain during the recovery. The actual L measurement was done at room temperature after a given recovery interval at 75 °C. To access the mechanism of UST effect on the diffusion length, we compared, on the same sample, the time constant of the post-UST recovery process and the Fe and B pairing kinetics. In the last case, both thermal dissociation of pairs at 200 °C for 5 min followed by quenching to room temperature by placing wafer on an aluminum plate, and optical dissociation provided by a halogen lamp (20 W/cm² at room temperature) were performed. The diffusion length kinetics of post-UST recovery and Fe-B pairing was expressed in terms of the ratio $\Delta(L^{-2})=(L^{-2}-L_1^{-2})/(L_0^{-2}-L_1^{-2})$, where L , L_0 , and L_1 are the time dependent, the initial, and the final value of diffusion length, respectively. The results are given in Fig. 2. The curves satisfy first order kinetics with time constants, τ , dependent on temperature, as shown in Table I. It is clear that both diffusion length recovery processes are characterized by similar τ values which are also close to calculated values obtained from Eq. (1). Therefore, we assert that Fe-B pairs were dissociated by UST applied to a silicon wafer and the liberated Fe_i ions subsequently participated in the regular pairing process.

The effect of UST on minority carrier diffusion length exhibited the following characteristics:

- the rate of a pair dissociation increased with an increase of the UST temperature in range of 55–100 °C. This indicates that the UST effect is temperature activated and the relevant time constant, τ_{UST} , decreases with increased temperature (see below);
- the L value showed only partial post-UST recovery (Fig. 1) this is consistent with the contribution from thermal pair dissociation which occurred when the wafer temperature increased to 75 °C (dashed line in Fig. 1); and

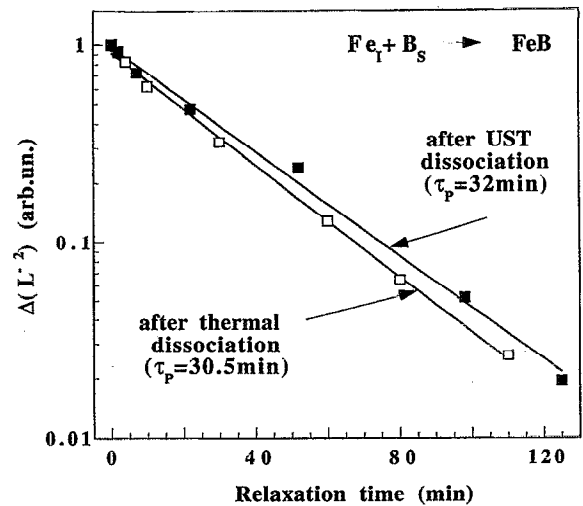


FIG. 2. Kinetics of post-UST relaxation and Fe-B pairing at 75 °C showing that both processes can be described by a first order reaction with similar time constants.

- by applying Eq. (2) to the results in Fig. 1, we determined that, at 75 °C, approximately 25% of Fe-B pairs were dissociated by UST.

The Fe-B pair concentration during UST and post-UST relaxation is described by the rate equation:

$$dN_{FeB}/dt = -R_D^{UST} - R_D^T + R_A^T = -N_{FeB}/\tau_{UST} - N_{FeB}/\tau_T + (N_0 - N_{FeB})/\tau_p, \quad (3)$$

where R_D^{UST} and R_D^T are the rates of ultrasound and temperature pair dissociation, respectively, and R_A^T is the rate of iron-boron pairing. Each of these pertinent processes is the first order reaction described by the respective time constant: τ_{UST} , τ_T , and τ_p . A solution of Eq. (3) can be obtained as a relative change of N_{FeB}/N_0 versus the effective time of UST expressed in units of “time/ τ_p ” using the parameters $\alpha=\tau_{UST}/\tau_p$ and $\beta=\tau_T/\tau_p$. A set of kinetic curves for the reaction of a pair dissociation is plotted in Fig. 3. The solid lines represent the effect of ultrasound breaking of FeB pairs when the temperature dissociation is neglected ($R_D^T=0$). The effect of R_D^T term is depicted by a broken line in Fig. 3 using the value of thermal dissociation rate evaluated from experiment (see below).

Using this approach, we fitted the experimental diffusion length points for UST and post-UST relaxation by solution of Eq. (3) as demonstrated in Fig. 1 (solid lines) using α and β as fitting parameters. The value of $\beta=\tau_T/\tau_p$ is directly related to the equilibrium fraction of FeB pairs: N_{FeB}/N_0

TABLE I. Kinetic time constants of post-UST recovery and Fe-B pairing compared to calculations [$[B]=5 \times 10^{14}$ cm⁻³ in Eq. (1)].

Temperature (°C)	Post-UST recovery (min)	Fe-B pairing (min)	Calculated value (min)
67	59	52	56.6
75	32	30.5	34.0
100	10	9	8.0

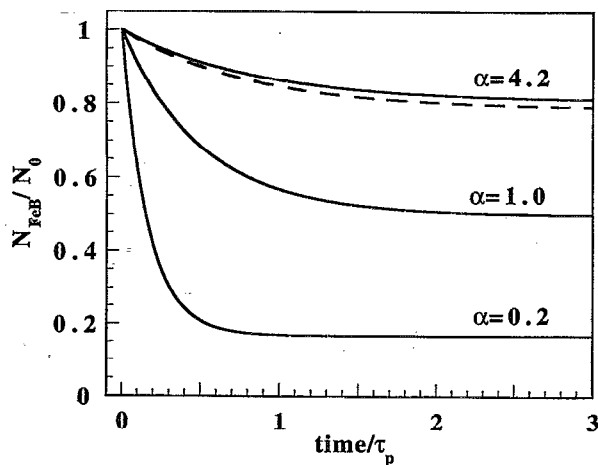


FIG. 3. Solutions of Eq. (3) for ultrasound dissociation of Fe-B pairs using parameters $\alpha = \tau_{UST}/\tau_p$ and $\beta = \tau_T/\tau_p$. The solid lines specify the UST effect of Fe-B pair breaking neglecting a temperature dissociation process ($\alpha \ll \beta$). The broken line represents a general solution of Eq. (3) with parameters used to fit the experimental data in Fig. 1 ($\alpha = 4.2$, $\beta = 30$).

$= \beta/(1 + \beta)$, which was accurately measured in *p*-type silicon as a function of temperature.^{6,10} This enabled us to compare our data with previously published results as shown in Table II (second column). Therefore, not only the pairing time constant, but also the time constant of a thermal dissociation process evaluated during our experiments, are consistent with well established results. Based on the agreement between experimental data and calculation we conclude that a simple physical model of the ultrasound stimulated dissociation of Fe-B pairs followed by a thermal association of Fe_i and B_s ions quantitatively describe diffusion length experiment.

We are not able at the present time to evaluate the activation energy of UST effect; however, it is obvious that τ_{UST}/τ_T ratio is increased with the elevation of temperature (Table II). Therefore, the activation energy is lower for the ultrasound enhanced dissociation process in comparison with temperature dissociation. This observation provides an important clue for a possible mechanism of UST effect. The ultrasound vibrations can transfer its elastic energy to anisotropic lattice defects like interstitial-substitutional pairs, using the mechanism of acoustically forced pair reorientation explored for Li-B pairs in Si.¹¹ It was shown that the "jump"

of an interstitial atom between two equivalent sites (nearest neighbors to the substitution atom) can occur in two steps. In the first step, interstitial atom moves to a distant interstitial site from substitutional atom, while, in the second step the mobile atom migrates to a new nearest-neighbor position accomplishing a reorientation process. The mechanism of pair reorientation is effective at the following resonance condition:¹²

$$2\pi f = \nu_0 \exp(\epsilon_a/kT), \quad (4)$$

where f is the operating frequency of the transducer, $\nu_0 = 10^{12} - 10^{13} \text{ s}^{-1}$ is the lattice phonon frequency, and ϵ_a is the pair binding energy. Substituting in Eq. (4) the parameters of UST ($f = 70 \text{ kHz}$ and $T = 75^\circ \text{C}$), we find the barrier $\epsilon_a = (0.44 - 0.51) \text{ eV}$. These values are close to a binding energy of 0.65 eV for FeB pair in silicon.⁸ The discrepancy can be attributed to a higher UST temperature required to overcome 0.65 eV barrier. This, however, would activate both temperature association and thermal dissociation of FeB pairs (reduction of τ_p and τ_T) and, as a consequence hide the UST effect. Therefore, we suggest that ultrasound vibrations can force a partial separation of Fe_i and B_s through the first step of resonance pair reorientation mechanism mentioned above. This reduces FeB pair binding energy and enhances the process of a complete pair dissociation.

The process of FeB pair dissociation under UST can account for a change of the diffusion length in a solar-grade polycrystalline silicon.⁴ Pair breaking followed by a capture of released Fe_i by sinks (dislocations, grain boundaries, precipitates) can be considered as a new approach in point defect gettering in silicon-based materials.

These authors would like to thank J. Lagowski for valuable discussion and critical reading of manuscript. We acknowledge helpful discussions of M. K. Sheinkman, G. D. Watkins, E. R. Weber, and J. Weber. This work has been supported by grants from National Renewable Energy Laboratory and Advanced Research Projects Agency.

TABLE II. Fitting parameters of UST-recovery experiment.

Temperature (°C)	Fraction of Fe-B pairs		τ_T/τ_p	τ_{UST}/τ_p
	Experiment	Calculation		
75	0.97	0.93	30	4.2
100	0.80	0.75	4	2.7

¹I. V. Ostrovskii and V. N. Lisenko, *Sov. Phys. Solid State* **24**, 682 (1982).

²V. L. Gromashevskii, V. V. Dyakin, E. A. Sal'kov, S. M. Sklyarov, and N. S. Khilimova, *Ukr. Fiz. Zh.* **29**, 550 (1984).

³S. S. Ostapenko, N. Ikeda, and F. Shimura, *Semiconductor Silicon*, edited by H. R. Huff, W. Bergholz, and K. Sumino, PV/94-10 (Electrochemical Society, Pennington, NJ, 1994), p. 856.

⁴S. S. Ostapenko, L. Jastrzebski, J. Lagowski, and B. Sopori, *Appl. Phys. Lett.* **65**, 1555 (1994).

⁵E. R. Weber, *Appl. Phys. A* **30**, 1 (1983).

⁶L. C. Kimerling and J. L. Benton, *Physica B* **116**, 297 (1983).

⁷G. Zoth and W. Bergholz, *J. Appl. Phys.* **67**, 676 (1990).

⁸J. Lagowski, P. Edelman, A. M. Kontkiewicz, O. Milic, W. Henley, M. Dexter, L. Jastrzebski, and A. M. Hoff, *Appl. Phys. Lett.* **63**, 3043 (1993).

⁹J. Lagowski, P. Edelman, M. Dexter, and W. Henley, *Semicond. Sci. Technol.* **7**, A185 (1992).

¹⁰H. Lemke, *Phys. Status Solidi A* **64**, 215 (1981).

¹¹B. S. Berry, *J. Phys. Chem. Solids* **31**, 1827 (1970).

¹²R. de Batist, *Internal Friction of Structural Defects in Crystalline Solids* (American Elsevier, New York, 1972), p. 67.