

# Increasing short minority carrier diffusion lengths in solar-grade polycrystalline silicon by ultrasound treatment

S. S. Ostapenko,<sup>a)</sup> L. Jastrzebski, and J. Lagowski

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

B. Sopori

National Renewable Energy Laboratory, Golden, Colorado 80401

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We have found that ultrasound treatment (UST) has a profound effect on the recombination rate in as-grown, B-doped cast polycrystalline silicon wafers for photovoltaic applications. As determined by surface photovoltage measurements of the minority carrier diffusion length  $L$ , the UST increases the corresponding lifetime by almost an order of magnitude. The maximum enhancement takes place in the wafer regions with the shortest  $L$  values. For  $L > 20 \mu\text{m}$ , both positive and negative changes of  $L$  after UST are revealed at different wafer regions. The UST effect is temperature dependent and exhibits maximum influence at about  $60^\circ\text{C}$ . Enhanced dissociation of Fe-B pairs by UST is identified as a mechanism which leads to a negative change of large  $L$  values, and a complex post-treatment relaxation. A positive change of  $L$  is attributed to the influence of ultrasound vibrations on crystallographic defects.

Ultrasound waves propagating in a semiconductor affect the properties of point and extended defects. A corresponding ultrasound treatment (UST) has been found to stimulate the following processes: (1) the generation of Frenkel pairs;<sup>1</sup> (2) the dissociation of point defect complexes;<sup>2</sup> and (3) enhanced gettering of point defects by sinks such as dislocations, grain boundaries, or precipitates.<sup>3,4</sup> It has been recognized that the sinks may serve as an efficient agent coupling the energy of ultrasound vibrations with extrinsic and intrinsic point defects.

The last group of processes are particularly important for UST of solar-grade polycrystalline silicon. The recombination properties of polycrystalline silicon, especially the minority carrier diffusion length,  $L$ , are controlled by point defects (e.g., heavy metal impurities) and extended lattice defects (grain boundaries and dislocations) interacting with each other. Cl and P gettering techniques are successful in increasing  $L$ , but only in wafer regions with relatively high  $L$  values, i.e.,  $L > 100 \mu\text{m}$ .<sup>5</sup> Regions with short diffusion lengths, where the crystallographic defects are the main recombination centers, are not affected by conventional gettering techniques. By analogy to other semiconductors with grain boundaries and dislocations,<sup>6</sup> UST may be an alternative technique to improve short diffusion lengths in polycrystalline silicon. In this letter, we report just such an observation for the first time.

Polycrystalline cast  $p$ -type silicon wafers (B-doped,  $2\text{--}10 \Omega \text{ cm}$ ) were studied. This material contains large single crystalline grains with surface areas ranging from a few  $\text{mm}^2$  to about  $1 \text{ cm}^2$ . We cut  $0.5\text{-mm-thick } 100 \times 100 \text{ mm}^2$  wafers to  $50 \times 50 \text{ mm}^2$  squares to match the size of a piezoelectric transducer (PZT-5H ceramics with Cr/Au electrodes up to  $74 \text{ mm}$  diameter) which was used as a source of ultrasound vibrations. The radial vibration mode (25 kHz for  $74 \text{ mm}$

transducer) or thickness vibration mode (590 kHz) were selected using the appropriate resonance frequency of a transducer. The transducers were driven by an ac voltage supplied from a functional generator coupled with a wideband power amplifier. For UST, the samples were either placed on the transducer and pressed to its surface using a spring contact or they were glued to the transducer. The UST is specified by the following parameters: (1) the amplitude of an acoustic strain generated by the transducer,  $\epsilon_{\text{us}} = 10^{-6}\text{--}10^{-5}$ , which is proportional to the applied ac voltage,  $V_{\text{us}} = 4\text{--}40 \text{ V}$ ; (2) the holding time,  $t_{\text{us}} = 10\text{--}60 \text{ min}$ ; (3) the temperature,  $T_{\text{us}} = 20\text{--}100^\circ\text{C}$  measured *in situ* with an infrared pyrometer; and (4) the frequency of ultrasound vibrations.

A commercially available, computer-controlled surface photovoltage (SPV) system for noncontact measurement of the minority carrier diffusion length  $L$ , and corresponding recombination lifetime,  $\tau = L^2/D$ , where  $D$  is the diffusion coefficient of the minority carriers (electrons in the present case), was used for mapping of  $L$  before and after UST. In calculating  $\tau$ , we used  $D = 32 \text{ cm}^2/\text{s}$  which corresponds to a low doping limit. Details of the SPV method are given in Ref. 7. The spatial resolution of the SPV mapping was  $2 \text{ mm}$  and the accuracy of the  $L$  measurements was better than  $1\%$ . Typically, a 177-point map or a line scan of 15 points was recorded before UST and after different types of UST on the same sample. Cast polycrystalline silicon wafers are strongly inhomogeneous.<sup>5</sup> Therefore, special precautions were undertaken to exactly compare the same wafer regions before and after UST. Iron concentration maps and profiles were determined using optical dissociation and thermal association of Fe-B pairs combined with  $L$  measurement as discussed in Refs. 8 and 9, respectively.

Two line scans of  $L$  before and after the UST are shown in Fig. 1. The increase in  $L$  in some regions is as high as a factor of 3. It is also seen that the strongest effect is observed for short initial  $L$  values. The temperature characteristic of the UST effect on  $L$  is given in Fig. 2. Consecutive isochro-

<sup>a)</sup>On leave from Institute of Semiconductor Physics, Academy of Sciences, pr. Nauki 45, Kiev, 252028, Ukraine.

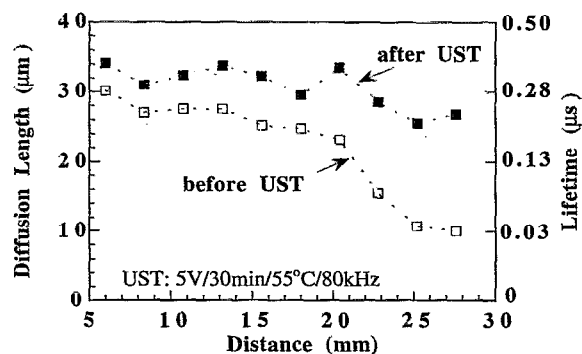


FIG. 1. Minority carrier diffusion length scans in solar-grade cast polycrystalline silicon before and after UST at 55 °C.

nal treatments were repeated at elevated temperatures. The maximum effect is for treatments between 55 and 65 °C. The results in Fig. 1 correspond to 55 °C, i.e., close to the optimum condition. For the sample in Fig. 1, the increase in  $L$  after the UST was permanent. By measuring a large number of different samples, we have found that this is not a general rule. Moreover, the change of  $L$  after UST shows significant differences, i.e., positive in some regions and negative in others as shown in Fig. 3.

Three subsequent UST were applied to the sample in Fig. 3, namely: UST1:  $V_{us}=40$  V,  $t_{us}=30$  min,  $T_{us}=40$  °C,  $f=48$  kHz; UST2: 55V, 30 min, 50 °C, 48 kHz; and UST3: 32 V, 80 min, 50 °C, 48 kHz. In Fig. 3(b) the positive change of  $\Delta L$  is observed for the wafer region with the shortest  $L$  values consistent with the behavior in Fig. 1. However, in Fig. 3(b), the negative  $\Delta L$  is also observed in some regions of higher initial  $L$  values.

In a kinetic study of UST procedures, we have identified three characteristics of the process: (1) the quantity  $\Delta(L^{-2})$  (which is proportional to the change of the concentration of recombination centers) satisfies the exponential dependence on the UST holding time,  $t_{us}:(\Delta L^{-2})=\Delta(L_0^{-2})[1 - \exp(-t_{us}/\tau)]$ ; (2) the magnitude of the effect,  $\Delta(L_0^{-2})$ , exhibits a maximum at a treatment temperature of about 60 °C

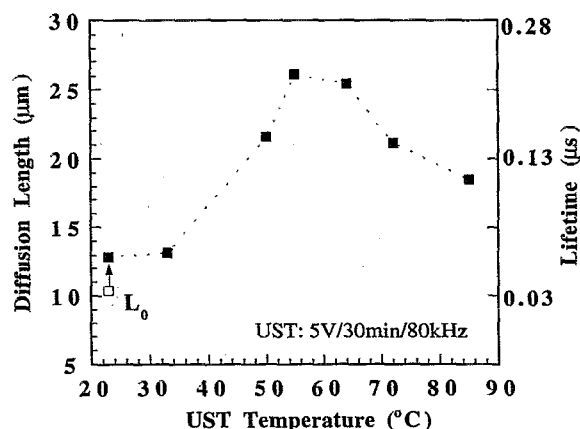


FIG. 2. Minority carrier diffusion length after UST vs treatment temperature.

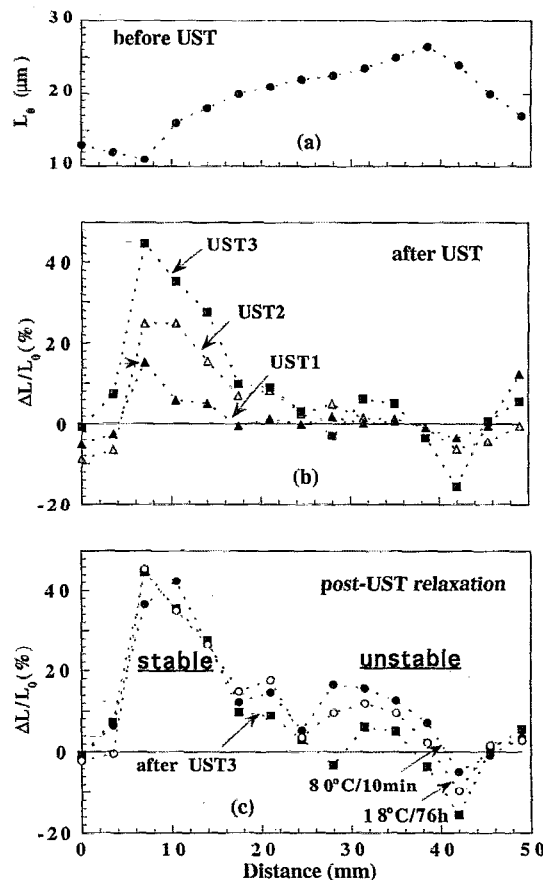


FIG. 3. Minority carrier diffusion length in polycrystalline silicon vs distance along the wafer: (a) before UST; (b) immediately after consecutive treatments; and (c) at various stages of post-treatment relaxation.

as illustrated in Fig. 2 by the behavior of  $\Delta L$  vs  $T_{us}$ ; and (3) the process time constant,  $\tau$ , is thermally activated with an estimated energy of  $(0.17 \pm 0.05)$  eV.

All of these characteristics of UST, observed for the case of recombination centers in polycrystalline silicon for the first time, are consistent with typical process features reported for compound semiconductors of group II-VI<sup>3,4,6</sup> and III-V.<sup>10</sup> For practical application of the UST effect as a means to increase  $L$ , the stability of the effect is of primary importance. As pointed out above, the effect is stable for short  $L$  values whereby the largest increase of  $L$  is also observed. In this "stable" range, as marked in Fig. 3(c), we found no noticeable relaxation of  $L$  after seven days at room temperature or after annealing of the sample for as long as 1 h at 80 °C. On the contrary, in the "unstable" range corresponding to larger  $L$  values and smaller relative  $L$  changes, we observed a new stable value. The relaxation exhibited complex behavior, however. It most frequently resulted in an increase of the  $L$  value during post-UST storage or low temperature annealing as shown in Fig. 3(c). This makes the UST a promising, practical tool for enhancement of diffusion lengths in solar-grade silicon.

The microscopic mechanisms of the  $L$  changes stimulated by UST are not presently known. The exact knowledge of recombination channels in solar-grade silicon, which con-

TABLE I. Fe-related effects of UST on diffusion lengths.

Dominant state of iron	Diffusion length $L$ ( $\mu\text{m}$ )		Mechanism
	Before UST	After UST	
$\text{Fe}_i\text{-B}^{\text{a}}$	53	42	UST stimulated pair dissociation
$\text{Fe}_i^{\text{b}}$	35	40	Thermal and/or UST pairing

<sup>a</sup>After 80 °C, 10 min. annealing.<sup>b</sup>After optical dissociation.

trol the  $L$  value, is not adequate for quantitative separation of contributions brought about by the precipitates, dislocations, grain boundaries, and impurities. Within the framework of this work, exploratory in scope, we were able to separate only the role of Fe. In B-doped  $p$ -type silicon, dissolved Fe tends to form electrostatically bonded  $\text{Fe}^+\text{-B}^-$  pairs which act as weak recombination centers for free excess electrons.<sup>9</sup> Dissociation of the pairs either thermally (200–250 °C annealing)<sup>9</sup> or optically (20 W/cm<sup>2</sup> of white light for 10 s)<sup>8</sup> at room temperature liberates interstitial iron,  $\text{Fe}_i^+$ , which is about a ten times more efficient recombination center than the Fe-B pair. Corresponding measurements of  $L$  before and after pair dissociation enable one to determine the concentration of Fe using available  $L$  vs  $[\text{Fe}]$  and  $L$  vs  $[\text{Fe-B}]$  calibration curves.<sup>9</sup> In addition, the low temperature ( $\sim 80$  °C) pair association kinetics provides a fingerprint of Fe separating its contribution from other pairs.<sup>8</sup>

In this work we have used the optical Fe activation method to measure Fe concentration maps and profiles. We have found that the wafer regions of negative  $\Delta L$  after UST coincide with a high initial concentration of Fe-B pairs of the order of  $10^{13}$  atoms/cm<sup>3</sup>. As shown in Table I, we could eliminate the negative  $\Delta L$  by dissociation of pairs prior to UST. After UST we could also achieve high  $L$  values in the same regions by short-term annealing at 80 °C (similar to that used to promote the pairing between  $\text{Fe}_i$  and B). Based on these findings, we conclude that UST most likely alters the reaction  $[\text{Fe-B}] \leftrightarrow \text{Fe}_i + \text{B}_s$ . In the case of high initial fraction of paired Fe, it causes ultrasound stimulated pair dissociation which decreases the  $L$  value. On the other hand, in the case of predominant dissociated pairs, it may promote the pairing reaction which increases the  $L$  value. Only the first of these two processes is unstable near room temperature.

To explain the ultrasound enhanced Fe-B dissociation process, we note that anisotropic point defects (i.e., donor-acceptor pairs) can demonstrate the reorientation by a jumping of the pair mobile component, usually an interstitial

atom, in the alternate elastic field of the ultrasound wave. An example of this mechanism is provided by the well-documented Li-B pair reorientation kinetics in silicon.<sup>11</sup>

The large increase in  $L$  observed in Figs. 1 and 2 in the sample regions with short initial  $L_0$  values cannot be associated with Fe-B pairs of  $\text{Fe}_i$ . Using the recombination parameters for Fe given in Ref. 9, we estimate that the reduction in Fe interstitial required to account for an increase in  $L$  from 10 to 27  $\mu\text{m}$  is about  $10^{14}$  atoms/cm<sup>3</sup>. This value exceeds, by an order of magnitude, the highest concentration of Fe-B pairs in the investigated wafers which was in the range of  $10^{12}$ – $10^{13}$  atoms/cm<sup>3</sup>. Thus, the stable increasing of short  $L$  must be related to other ultrasound stimulated processes, perhaps the enhanced gettering of point defects previously reported in Refs. 3 and 4.

In conclusion, we have shown that the UST offers an effective means for defect engineering in polycrystalline silicon cast material which can constitute a promising new technique to increase the minority carrier diffusion length, especially in regions with short  $L$  values. We have also provided empirical evidence for ultrasound stimulated dissociation of Fe-B pairs.

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