

SEMICONDUCTORS AND DIELECTRICS

Ultrasound-Stimulated Increase in the Electron Diffusion Length in *p*-Si Crystals

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Abstract—The effect of ultrasound on the diffusion length of minority charge carriers in dislocation-free *p*-Si is investigated in the frequency range 0.8–5.5 MHz. The diffusion length is measured by the surface photovoltage method. It is found that the diffusion length reversibly increases (by a factor of two at a sound intensity of 3 W/cm²) in response to ultrasound. The dependences of the diffusion length on the ultrasound amplitude and the kinetic characteristics upon switching on and switching off the ultrasound are analyzed. The phenomena observed are explained within the proposed model of transformation of recombination centers under the effect of ultrasound. © 2002 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

It is known that intense ultrasonic waves propagating in solids substantially affect the state of structural defects [1–6]. For example, the ultrasound effect brings about the formation of a surface layer in silicon [1] and the dissociation of complex aggregates consisting of several point defects [2], enhances gettering of point defects by dislocations and precipitates [3], and decreases the energy barrier to defect diffusion [4–6]. Considerable progress toward physical understanding of the ultrasound effect has been achieved by elucidating the dislocation mechanism of the acousto-defect interaction [4, 6, 7]. However, dislocation-free solids remain poorly investigated.

In the present work, we analyzed how the ultrasound affects silicon single crystals prepared from *Cz-p*-Si (solar-cell grade). The results obtained are essential to the understanding of the mechanism of the physical processes associated with the interaction of ultrasonic waves and a subsystem of point defects in dislocation-free semiconductor crystals.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

The effect of ultrasound on the diffusion length L of minority charge carriers in *Cz-p*-Si was investigated using boron-doped *p*-Si(100) wafers 340 μm thick ($\rho = 0.5\text{--}2\ \Omega\text{ cm}$) with an oxygen concentration $N_O \leq 10^{18}\text{ cm}^{-3}$ and a carbon concentration $N_C \leq 10^{17}\text{ cm}^{-3}$. According to x-ray diffraction analysis, the dislocation density was less than 10 cm^{-2} ; i.e., the samples were virtually free of dislocations.

The diffusion length was measured by the surface photovoltage method [8, 9]. This method is based on analyzing the dependence of the surface photovoltage V_{sp} on the monochromatic light wavelength. The advan-

tage of the surface photovoltage method is its applicability under the conditions of variations in the carrier concentration in the sample [10]. Figure 1 depicts a schematic drawing of the experimental cell. The surface photovoltage V_{sp} was measured by the capacitor method with the use of an electrode applied on the sample surface opposite to the illuminated surface. The experiments were performed at room temperature.

In semiconductor wafers, ultrasonic vibrations were excited by ceramic (TsTS-19) piezoelectric transducers cemented to the sample. An ac voltage with a frequency $f = 0.8\text{--}5.5\text{ MHz}$ and an amplitude V_{us} up to 40 V was applied to one of the piezoelectric transducers to generate acoustic vibrations in the silicon sample. The generation of acoustic vibrations was controlled by another

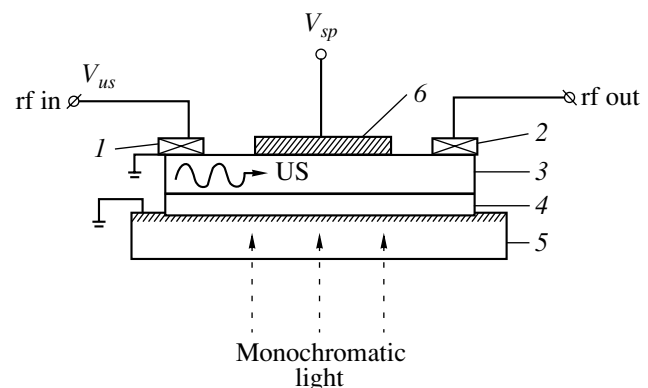


Fig. 1. A schematic drawing of the experimental cell for measuring the diffusion length of minority charge carriers in a semiconductor wafer in an ultrasound field: (1, 2) piezoelectric transducers, (3) silicon sample, (4) mica, (5) glass with an applied transparent electrode, and (6) metal electrode for recording the photovoltage.

piezoelectric transducer mounted at the opposite end of the silicon sample. The ultrasonic waves induced in the sample were identified as Lamb waves (the a_0 and s_0 modes) on the basis of the measured wave velocities.

The intensity W_{us} of ultrasound generated in the sample was approximately equal to 0.5 W/cm^2 at $V_{us} = 10 \text{ V}$ and $f = 0.8 \text{ MHz}$.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The diffusion length of minority charge carriers (electrons) was measured in the absence of ultrasound and after its generation. In the absence of ultrasound, the initial diffusion length L_0 in the p -Si samples under investigation is equal to $15\text{--}25 \text{ }\mu\text{m}$. The ultrasound effect leads to an increase in the diffusion length L by 100% at maximum sound intensities. It should be noted that all ultrasound-stimulated changes are reversible; i.e., after switching off the ultrasound, the parameters of the material regain their original values for some time.

The characteristic dependences of the relative change in the diffusion length L on the time of ultrasonic treatment are displayed in Fig. 2. The observed behavior of the time dependence of the diffusion length L —an increase after the ultrasound is switched on (portion ab) and a decrease after it is switched off (portion bc)—is typical of all the frequencies and amplitudes of the ultrasound used. The maximum diffusion length L_{us} is reached for an ultrasonic treatment time of $5 \times 10^3 \text{ s}$ and depends on the ultrasound intensity. Figure 3 shows typical dependences of the diffusion length L_{us} on the

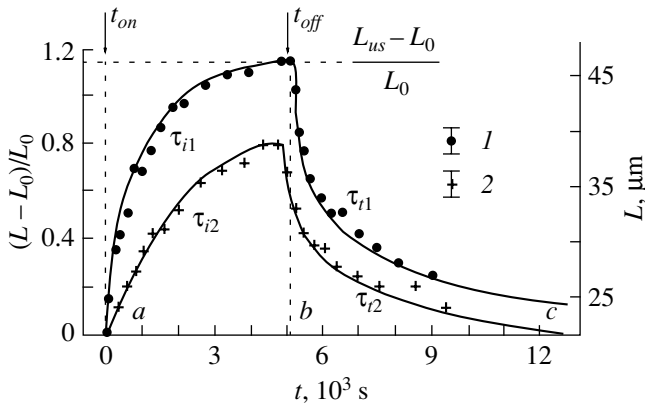


Fig. 2. Time dependences of the diffusion length: increase (portion ab) after switching on the ultrasound ($t = t_{on}$) and decrease (portion bc) after switching off the ultrasound ($t = t_{off}$). $f = 0.78 \text{ MHz}$. $V_{us} = (1) 35$ and $(2) 25 \text{ V}$. The diffusion length L_0 in the absence of ultrasound is equal to $22 \text{ }\mu\text{m}$. $\tau_{i1} < \tau_{i2}$ and $\tau_{i1} = \tau_{i2}$.

ultrasound intensity W_{us} . It can be seen that the sound-stimulated increase in the diffusion length L is characterized by a threshold at $W_{us} \approx 0.5 \text{ W/cm}^2$ and saturation at higher ultrasound intensities ($>2 \text{ W/cm}^2$). Moreover, there is a pronounced hysteresis. It is seen that the dependence $L_{us}(W_{us})$ follows the curve $ABCD$ in the course of the initial ultrasonic treatment and the curve $AFED$ in subsequent cycling. The initial dependence ($ABCD$) can be regained if the samples are allowed to stand for two or three weeks at room temperature.

During ultrasonic treatment, the temperature of the silicon wafer was monitored using a copper–constantan thermocouple. It was found that, at a maximum ultrasound intensity, the sample temperature increased by $15\text{--}18 \text{ K}$. After check heating of the silicon sample by 18 K in the absence of ultrasound, the diffusion length L increased by less than 10%. Note that the measured temperature dependence of the diffusion length L agrees with the data obtained in [11] to within the experimental error in the measurement of the length L ($5\text{--}7\%$).

As is known, the charge carrier recombination in silicon at moderate degrees of doping ($<10^{18} \text{ cm}^{-3}$) and at room temperature predominantly proceeds through deep levels [12, 13]. Under the assumption that the above mechanism of charge carrier recombination remains dominant in a crystal subjected to ultrasonic treatment, we can write the following relationship in the framework of the Shockley–Read–Hall model:

$$L^{-2} = D^{-1} v_T \sum_k S_k N_k, \quad (1)$$

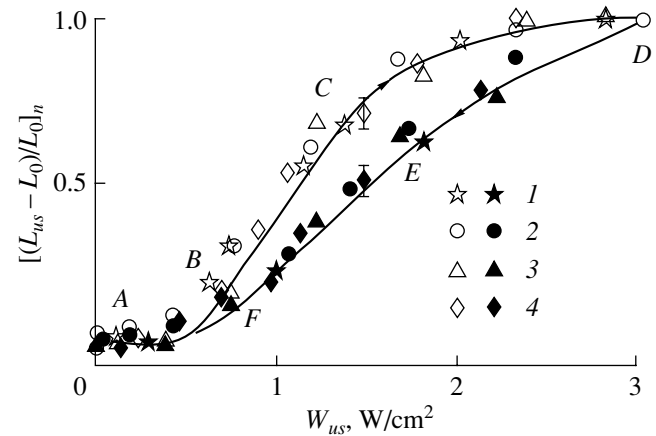


Fig. 3. Dependence of the diffusion length on the ultrasound intensity. The data obtained in the initial and subsequent ultrasonic treatment cycles are represented by open and closed symbols, respectively. Different types of symbols indicate the results obtained at different ultrasonic frequencies for different samples. $f = (1\text{--}3) 0.78$ and $(4) 1.8 \text{ MHz}$. The ratio $[(L_{us} - L_0)/L_0]_n = 1$ corresponds to $(L_{us} - L_0)/L_0 = (1) 1.2$, $(2) 1.15$, $(3) 0.95$, and $(4) 0.48$.

where D is the diffusion coefficient of electrons, v_T is the thermal velocity of electrons, and S_k and N_k are the capture cross section and the concentration of the k th recombination centers, respectively. From relationship (1), it follows that the reciprocal of the diffusion length squared is directly determined by the parameters of the deep levels involved and that the change in the length $\Delta L^{-2} \equiv L_0^{-2} - L^{-2}$ is proportional to the change in $(S_k N_k)$, because, under the experimental conditions, the product $(D^{-1} v_T)$ remains virtually constant. On this basis, the ascending and descending portions of the curve $L(t)$ (portions ab and bc in Fig. 2) can be described by the expressions

$$\Delta L_i^{-2} = \Delta L_{us}^{-2} [1 - \exp(-t/\tau_i)], \quad (2)$$

$$\Delta L_t^{-2} = \Delta L_{us}^{-2} \exp(-t/\tau_t), \quad (3)$$

where $\Delta L_{us}^{-2} \equiv L_0^{-2} - L_{us}^{-2}$ and τ_i and τ_t are the characteristic times of changes in the system of recombination centers in the cases of an increase (ΔL_i) and decrease (ΔL_t) in the diffusion length of minority charge carriers, respectively. It should be noted that expressions (2) and (3) are standard equations used for first-order kinetic processes. According to expressions (2) and (3), we can write the following relationships:

$$F_i \equiv \ln \left(\frac{L_0^2 L_{us}^2 - L^2}{L^2 L_{us}^2 - L_0^2} \right) = -\frac{t}{\tau_i}, \quad (4)$$

$$F_t \equiv \ln \left(\frac{L_{us}^2 L^2 - L_0^2}{L^2 L_{us}^2 - L_0^2} \right) = -\frac{t}{\tau_t}. \quad (5)$$

The time dependences of F_i and F_t at different amplitudes V_{us} are shown in Figs. 4a and 4b, respectively. As is seen from these figures, the dependences $F_i(t)$ and $F_t(t)$ are well approximated by straight lines whose slopes can be used to determine the characteristic times τ_i and τ_t . The calculations demonstrate that the characteristic time τ_i depends on the ultrasound amplitude, whereas the time τ_t is independent of this parameter. In subsequent ultrasound switching-on and switching-off cycles, the characteristic times τ_i and τ_t remain unchanged.

Let us analyze the observed dependence of the characteristic time τ_i on the ultrasound amplitude within the diffusion theory of transformation of recombination centers. In the general form, the characteristic relaxation time τ for a system of recombination centers can be represented as

$$\tau = \tau_0 \exp(E_a^0/kT), \quad (6)$$

where E_a^0 is the activation energy of the process which results in a change in the diffusion length L (for exam-

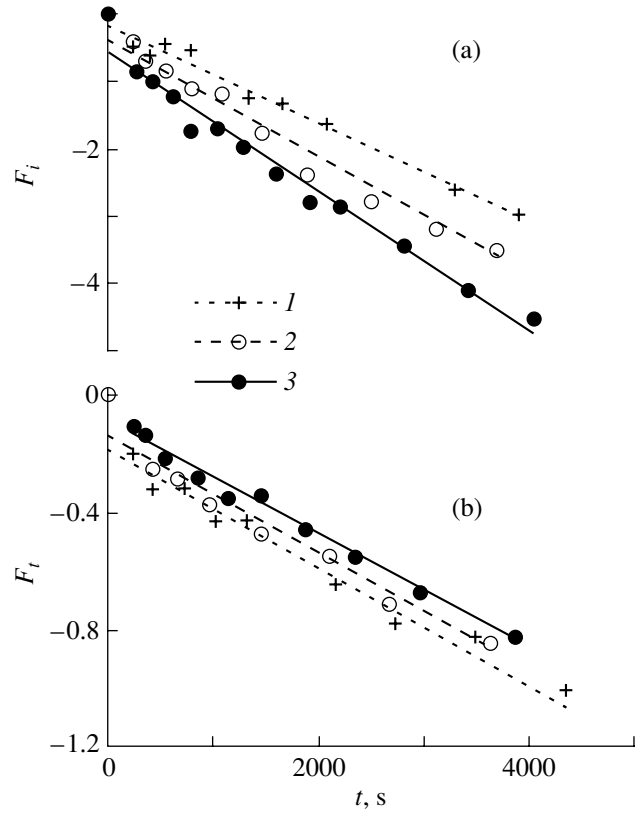


Fig. 4. Time dependences of (a) F_i and (b) F_t [see relationships (4) and (5)] at different amplitudes V_{us} : (1) 25, (2) 30, and (3) 35 V. $f = 0.78$ MHz. The characteristic relaxation times τ_i and τ_t calculated from the slopes of the dependences $F_i(t)$ and $F_t(t)$ are as follows: $\tau_i = (1) 21$, (2) 16, and (3) 15 min and $\tau_t \approx (1-3) 80$ min.

ple, diffusion of atoms or ions involved in defects) and τ_0 is a constant which is the reciprocal of the thermal relaxation frequency. Under the conditions of mechanical loading of the crystal, the change in the activation energy E_a^0 can be approximated by a linear dependence [4, 6, 14]: $E_a = E_a^0 - \gamma\sigma$, where σ is the mechanical stress and γ is a certain activation volume. In our case of ultrasonic treatment of the crystal, we have $\sigma_{us} = (2\rho_s v_{us} W_{us})^{1/2}$ (where ρ_s is the silicon density and v_{us} is the ultrasonic wave velocity) and the parameter γ has the meaning of the effective coefficient of interaction between ultrasonic waves and crystal defects.

As a consequence, under the conditions of ultrasonic treatment, we obtain the following expression for the characteristic relaxation time:

$$\tau = \tau_0 \exp((E_a^0 - \gamma\sigma_{us})/kT). \quad (7)$$

Expression (7) permits us to evaluate the parameter γ . The experimental dependence of the characteristic relaxation time τ on σ_{us} is depicted in Fig. 5. The parameter γ was determined from the slope of the

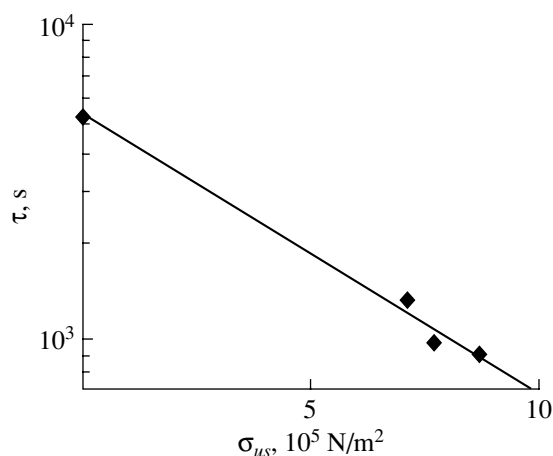


Fig. 5. Dependence of the relaxation time on the mechanical stress in an ultrasound field.

straight line in this figure: $\gamma = (8 \pm 2) \times 10^{-27} \text{ m}^3$. The obtained value of γ corresponds to an effective acousto-defect interaction range of 12 Å, which is comparable to the lattice parameter. This can be associated only with point defects (including their complexes). The physical meaning of the parameter γ can be defined as the effective volume of interaction between the elastic field of a complex defect and ultrasonic vibrations.

4. A POSSIBLE MECHANISM OF THE ULTRASOUND EFFECT

When analyzing the possible mechanisms of the ultrasound effect on the diffusion length in silicon of solar-cell grade, proper allowance must be made for the following factors: (i) the relatively small initial diffusion lengths L_0 (of the order of tens of microns), which suggests a high concentration of recombination centers (of the order of 10^{13} – 10^{14} cm^{-3}); (ii) the long-term (of the order of tens of minutes) transient processes after switching on and switching off the ultrasound, which is characteristic of the diffusion mechanism of transformation of defect structures [4]; and (iii) the reversibility of the amplitude and time changes.

The experimental data obtained can be interpreted in the framework of the model of a bistable acoustoactive recombination center. Within this model, it is assumed that a defect can exist in two stable states (*A* and *B*) with different carrier capture cross sections (for example, $S_A > S_B$). In the absence of ultrasound, the probability of finding the defect in the *A* state is higher than that in the *B* state. After switching on the ultrasound, a number of defects transform into the *B* state. Consequently, the recombination rate decreases as the result of a decrease in the capture cross section. After switching off the ultrasound, the system of defects reverts to the original state. In silicon, the system of defects can consist of pairs, each formed by a dopant

atom and an interstitial metal atom, for example, Cr–B, Fe–B, and Fe–Al pairs whose bistability has long been known [15–17]. It should be emphasized that it is these heavy metal impurities which are responsible for the considerable decrease in the diffusion length of minority charge carriers [11, 12].

As an example, we consider an iron–boron pair. The presence of iron at a concentration of 10^{13} – 10^{14} cm^{-3} in silicon leads to a decrease in the diffusion length L_0 to 20 μm [11, 12]. At room temperature, iron atoms in Si:B are almost completely bound in $\text{Fe}_i\text{--B}_s$ complexes [18]. The bistability of these complexes stems from the fact that the iron ion can occupy either the *T* interstice nearest to the B atom (configuration *A*) or the next-nearest interstice (configuration *B*) [16]. In a pair with configuration *B*, the spacing between the two energy levels that correspond to the two charge states Fe^{2+} and Fe^+ is smaller by 0.14 eV [16]. Within the model under consideration, the sound-stimulated transition of a complex from the *A* state to the *B* state can be treated as diffusion of the interstitial iron ion from one interstice to another interstice in an ultrasound field, followed by the recharging $\text{Fe}^{2+} \rightarrow \text{Fe}^+$ in a number of defects until thermodynamic equilibrium between different charge states is attained. A decrease in the fraction of Fe^{2+} ions should lead to a decrease in the electron capture cross section and a subsequent increase in the diffusion length L . In the ultrasound field, the diffusion of impurity atoms is stimulated by their interaction with nonequilibrium phonons excited by ultrasonic waves [19]. The recharging of ions with a change in their spatial position was described in [20].

In order to verify the validity of the model described above, we performed experiments with illumination of the samples under investigation. According to Lagowski *et al.* [10], sufficiently intense illumination ($\sim 10 \text{ W/cm}^2$) of silicon crystals with white light at room temperature brings about the decomposition of pairs of the Fe–B type. In turn, this leads to a decrease in the diffusion length of minority charge carriers, because the electron capture cross section of interstitial iron ions is larger than that of the $\text{Fe}_i\text{--B}_s$ pair. Illumination of the studied samples in the absence of ultrasound causes the diffusion length L to decrease by approximately 15%. In the case when the samples are illuminated in the course of ultrasonic treatment, the diffusion length decreases to a considerably larger extent and the ultrasound-stimulated increase in the diffusion length is virtually suppressed under exposure to light. In the framework of the proposed model, this fact is explained by the photoinduced decomposition of the pairs.

Furthermore, silicon contains other defects that can participate in the acousto-defect interaction, namely, complexes involving vacancies. In particular, a vacancy–boron pair can be considered a bistable defect [21]. In this case, different configurations of the vacancy complex with a dopant atom exhibit significantly different recombination properties due to partial

internal charge redistribution [22]. Therefore, the ultrasound-induced transition in this defect should result in a change in the diffusion length L .

5. CONCLUSIONS

Thus, the results obtained in the present work can be summarized as follows.

(1) The reversible increase in the diffusion length of electrons in dislocation-free p -Si crystals under the effect of ultrasound is observed for the first time.

(2) The effective volume of the acoustodefekt interaction is estimated as $\gamma = (8 \pm 2) \times 10^{-27} \text{ m}^3$. This indicates that the ultrasonic waves interact with point defects.

(3) A model of ultrasound-induced transformation of recombination centers in a silicon crystal is proposed. Consideration is given to the possible ultrasound-induced transformations in different defects, namely, pairs containing impurity atoms located at sites and interstices and complexes involving vacancies.

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