J. Phys. D: Appl. Phys. **41** (2008) 165107 (7pp) doi:10.1088/0022-3727/41/16/165107

Open-circuit voltage decay transient in dislocation-engineered Si p–n junction

A Davletova[1] **and S Zh Karazhanov**[1,2]

[1] Physical-Technical Institute, 2B Mavlyanov St., 700084 Tashkent, Uzbekistan
[2] Institute for Energy Technology, PO Box 40, NO-2027 Kjeller, Norway

Received 18 January 2008, in final form 28 May 2008
Published 30 July 2008
Online at stacks.iop.org/JPhysD/41/165107

Abstract
This work presents a study of an open-circuit voltage decay transient in dislocation-engineered Si p–n junctions. It is found that upon switching off the illumination the open-circuit voltage decreases with time according to the exponential function, whereas the excess carrier concentration decreases with time according to the double exponential function. This result indicates that the dislocation-engineered Si p–n junctions are sensitive to variations of the band-to-band illumination intensity. It is found that the carrier lifetime and open-circuit voltage can be modulated by ultrasound treatment.

1. Introduction

Due to its indirect band gap Si is a poor light-emitting material. However, extensive applications of this material in semiconductor electronics require enhancement of light emission from Si [1]. Dislocation engineering (DE) is found to enhance the luminescence properties of Si in boron-implanted Si [2–4], hydrogen- and helium-implanted Si [5–7]. Gettering and passivation [8, 9] of electrically active defects decorating the dislocations can also be useful for these purposes. The strain field around the dislocation loops provides spatial confinement of charge carriers, accumulates impurities and defects and modulates carrier recombination and, thus, transient behaviour of electrical parameters of DE Si. So far, attention has basically been paid to the study of luminescent properties of Si. However, transient of electrical parameters of the DE Si such as, e.g., open-circuit voltage, is open.

The open-circuit voltage (V_{oc}) decay transient has previously been studied experimentally and theoretically in dye-sensitized solar cells (DSSCs) using poly(3,4-ethylenedioxythiophene) as hole conductors [10], DSSC with and without TiO_2 blocking underlayers [11–17], GaAs light-emitting diodes [18] and crystalline and amorphous Si [19,20]. It is found [11–17] that V_{oc} can decay according to the exponential function. However, in some dislocation-free solar cells V_{oc} is found [21–24] to decrease linearly with time after the illumination is switched off.

As noted above, defects and impurities can be accumulated around dislocations, which can increase the non-radiative recombination rate of charge carriers and thus quench the dislocation-related illumination. To avoid it, passivation by H or annealing at high temperatures can be used. However, after annealing at temperatures higher than 200 °C luminescence of DE Si can be completely quenched [4]. This problem created the necessity to find alternative ways of annealing DE Si at moderate temperatures without destroying its luminescence properties. Ultrasound treatment (UST) could be used for annealing at lower temperatures <200 °C [25–27]. According to the scientific literature, UST has successfully been used so far for metal cluster engineering in ion implanted silicon dioxide [28], defect engineering in Si p–n junctions [29], extension of the spectral sensitivity of the AlGaAs/GaAs solar cells towards short-wave lengths [30], modification of radiation-induced defects in Si [31], etc. The aim of this paper is to study an open-circuit voltage decay transient in DE Si before and after the UST.

2. Experimental details

2.1. Sample characteristics

The measurements have been performed for the S doped dislocation-engineered Si p–n junction diodes (figure 1) obtained from the Advanced Technology Institute, School of Electronics and Physical Sciences, University of Surrey, Guildford, UK. The samples have been fabricated by boron implantation into Czochralski (CZ) n-type Si with a contact area of 1.76 mm^2 and width of 1.00 mm, respectively. The presence of boron-implantation induced dislocation loops has been detected by TEM analysis [32–34].

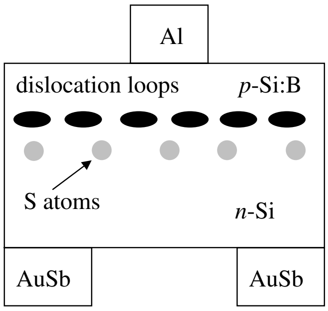

Figure 1. A schematic diagram of the structure of the sulfur doped Si dislocation-engineered p–n junction.

Table 1. Sulfur implantation dose D (cm^{-2}), annealing temperature T (°C) to activate the sulfur atoms, UST time τ_{UST} (min) and UST power P (W cm^{-2}).

Samples	D (cm^{-2})	T (°C)	τ_{UST} (min)	P (W cm^{-2})
B1	10^{13}	1100	15	1.0
B2			30	1.0
B3			30	0.5
B4			15	0.5
A1	10^{14}	1000	15	1.0
A2			30	1.0
A3			30	0.5
A4			15	0.5
C1	0	0	15	1.0
C2			30	1.0
C3			15	0.5
C4			30	0.5

Three groups of samples denoted by A1–A4, B1–B4 and C1–C4 have been studied (table 1). S impurities have been implanted into A1–A4 samples of dose 10^{14} cm^{-2} with an annealing temperature of 1000 °C and B1–B4 samples of dose 10^{13} cm^{-2} with rapid thermal annealing at 1100 °C. The C1–C4 samples do not contain S impurities. More details on the preparation of samples can be found elsewhere (see, e.g., [32–34]).

2.2. UST and open-circuit voltage decay transient measurements

The UST of the samples has been performed from the contact side by a ceramic piezoconvertor. The frequency of the UST was 2.4 MHz. The UST has been done in alcohol. Samples have been treated by ultrasound of powers 0.5 and 1.0 W cm^{-2} for 15 and 30 min (table 1).

The open-circuit voltage (V_{oc}) decay transient has been measured. During the measurements contacts have darkened. The sample was illuminated by light pulses of the light-emitting diode A1-402 of wavelength $\lambda = 0.69\,\mu$m. The power of the LED is 5 mW. The reason for the choice of the low power is related to the sensitivity of the samples to variations of the illumination intensity. All measurements have been performed at room temperature.

Cables of type RK-75 have been used in the measurements with a wave resistance of 75.0 Ω and a capacity of 7.6 pF. The capacity of the voltmeter is 1.0 pF. In total the capacitance of the experimental setup is ∼10 pF. From the study of capacitance/voltage characteristics before and after the UST for different frequencies it is found that the capacitance of the measured space charge is much larger than that of the experimental setup.

The input resistance of the voltmeter is 1 MΩ; the resistance of the samples is also ∼1 MΩ. the input capacitance of the experimental setup is $C = 1$ pF. As demonstrated later, the characteristic time of the sample–voltmeter combination is much shorter than the smallest decay time of the open-circuit voltage, which is in the range 15–190 μs.

2.3. Theory and assumptions

Upon illumination free electrons and holes are generated, which can be separated by the potential barrier of the p–n junction, and thus an open-circuit voltage has been generated. When the illumination is switched off, the excess carrier concentration is decreased because of the electron–hole recombination. The decrease can be described by the following equation [13, 14]:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -U = -\frac{n - n_0}{\tau}. \tag{1}$$

Here n_0 and n are the equilibrium and non-equilibrium electron concentrations in the region of p-type conductivity to be called hereafter the p region. t and τ are the time and the carrier lifetime, respectively. U is the carrier recombination rate. Commonly U is a nonlinear function of n and it can be presented as $U = (n - n_0)/\tau$. Here τ is not constant; it nonlinearly varies with n. The rate at which the open-circuit voltage decays with time depends on the dynamic exchange of electrons between the conduction and valence bands. The non-equilibrium carrier concentration n has been estimated using the measured open-circuit voltage (V_{oc}):

$$n = n_0 \times \exp\left(\frac{qV_{oc}}{\beta kT}\right). \tag{2}$$

Here T is the temperature, k is the Boltzmann constant and q is the electron charge. β is known as the ideality factor. After the illumination is switched off, V_{oc} decreases with time. The decay transient of V_{oc} has been used to estimate the carrier lifetime [8].

3. Results and discussion

3.1. Open-circuit voltage decay

Figure 2 presents an open-circuit voltage decay transient for the dislocation-engineered Si p–n junction before and after UST. It is interesting to note that for all samples the time dependence of V_{oc} can be described by the exponential function:

$$V_{oc}(t) = V_{oc}(0) \times \exp\left(-\frac{t}{\tau_0}\right). \tag{3}$$

The function $V_{oc}(t)$ in equation (3) has been nicely fitted to the experimental data in figure 2 plotted by symbols. In this way, the characteristic time τ_0 has been determined, which

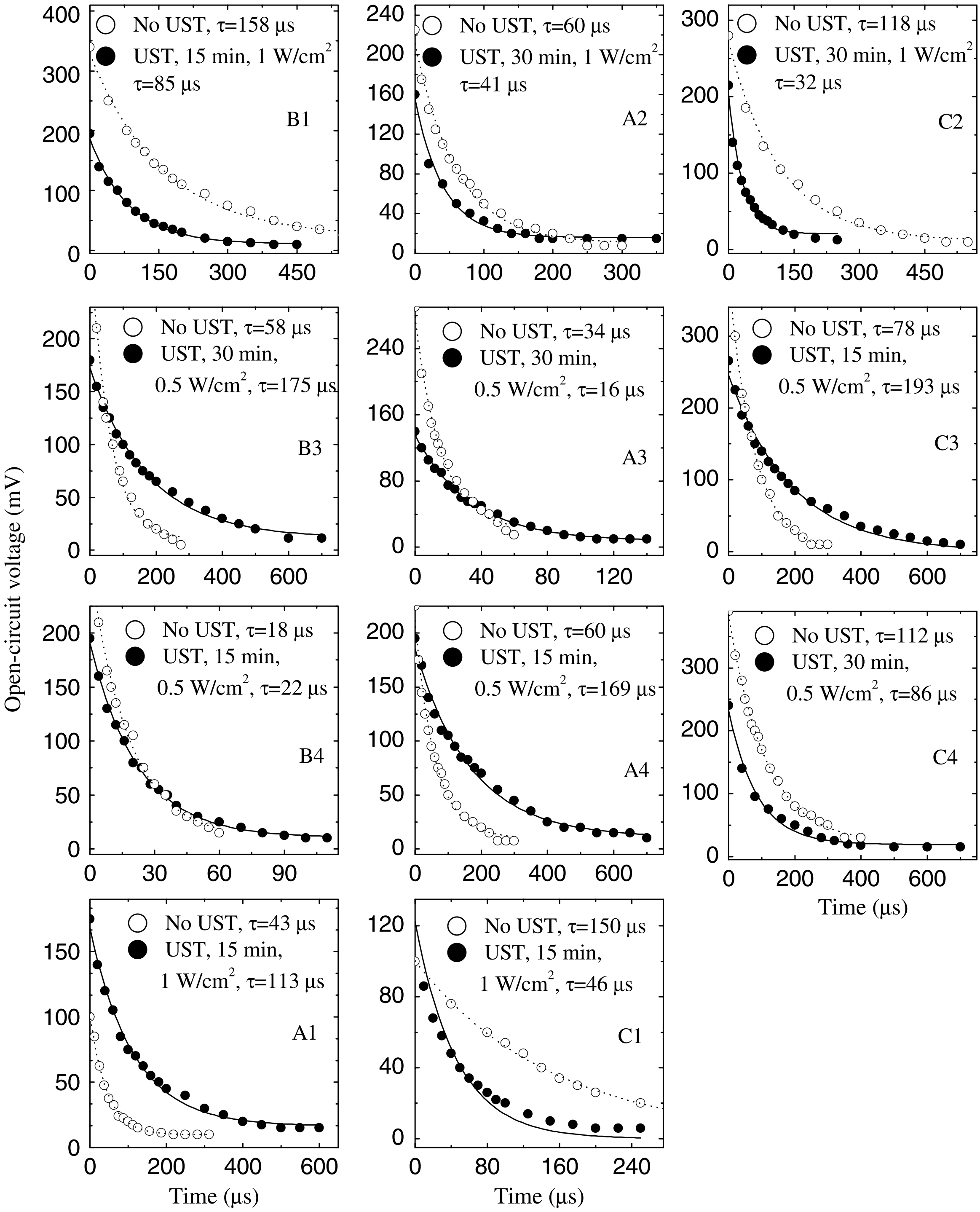

Figure 2. Experimentally measured open-circuit voltage decay transients before (○) and after (●) UST. Broken and full lines correspond to data fitted by equation (3). The labels A1–C4 denote the samples listed in table 1.

is presented in the inset of each figure of figure 2. As we show later, the characteristic time τ_0 is the carrier lifetime in equation (1), i.e. for the non-equilibrium stationary case characterized by a high carrier concentration. It can also be called the response time of the device [8,9,35]. The analysis of figure 2 shows that the values of τ_0 measured in this work are one–two orders of magnitude larger than the 1.8 μs of room-temperature Si dislocation-related light-emitting diodes [2]. However, they are of the same order as that of [36].

All the samples have been treated by ultrasound. The UST has not changed the exponential character (equation (3)) of the open-circuit voltage decay transient. However, the characteristic decay time τ_0 has been changed drastically. In five samples UST resulted in an increase in τ_0 1.33–575.00 times. Consequently, in these samples the response time of the DE p–n junction to external illumination has been decreased. In the remaining six samples the UST resulted in a decrease in τ_0 1.53–6.52 times, thus giving a faster response of the p–n junction to variations of the illumination intensity. The UST induced-decrease in τ_0 indicates UST-stimulated formation of defects increasing the carrier recombination rate and, respectively, reducing the carrier lifetime. Hence, the UST can worsen the electrical parameters of the p–n junction. The UST-enhanced increase in τ_0 can be related to UST-induced reduction in the concentration of recombination active defects thus resulting in the improvement of the carrier lifetime. Consequently, UST can be useful to anneal the recombination active defects. As well known, the UST-induced formation and annealing of defects in the DE Si p–n junction can be controlled by UST power, duration and frequency. This result is the first demonstration of the effect of UST on the DE Si p–n junction.

The analysis of figure 2 shows that as a result of the UST the magnitude of V_{oc} at $t = 0$ has been considerably decreased for all the samples except the one in figure 2(*h*). Since according to the theory of solar cells [27] V_{oc} can be controlled by the carrier concentration, one can ascribe the UST-induced decrease in $V_{oc}$to that of the equilibrium free carrier concentration. The latter is well known to be related to the formation of deep level defects capturing the free carriers.

It should be noted also that the open-circuit voltage transients before and after UST differ from each other. The difference can be ascribed to UST-induced modulation of the defect spectra around the dislocations, which influences the dynamics of carrier exchange between the conduction and valence bands. The UST-induced difference in the V_{oc} decay transient indicates that depending on the UST power and the duration different kinds of defects can be formed, which can be responsible for the modulation of kinetics of generation–recombination processes. This result is consistent with findings regarding UST-induced modulation of radiation defects in ionic crystals CsI and KBr [25], room-temperature annealing of radiation defects in Si by ultrasound [37], decomposition of the point defect complexes [38], gettering of point defects by dislocations and precipitates [39], reducing the barrier height for defect diffusion [10], etc.

As noted in the introduction, the open-circuit voltage decay transient according to the exponential function (equation (3), figure 2) has previously been observed experimentally in DSSC using poly(3,4-ethylenedioxythiophene) as hole conductors [11–17], DSSC with and without TiO_2 blocking underlayers [11–17], GaAs light-emitting diodes [18] and crystalline and amorphous Si [19, 20]. To our knowledge this is the first study of the open-circuit voltage decay transient in DE Si and we demonstrated the possibility of exponential decay of $V_{oc}(t)$. However, the results in figure 2 are different from those observed in some dislocation-free solar cells with a linear decrease in $V_{oc}(t)$ after the illumination is switched off [21–24]:

$$V_{oc}(t) \propto -t. \tag{4}$$

Commonly, the dependence $V_{oc}(t)$ described by equation (4) causes an exponential decrease in the carrier concentration [21]:

$$n(t) \propto \exp\left(-\frac{t}{\tau}\right). \tag{5}$$

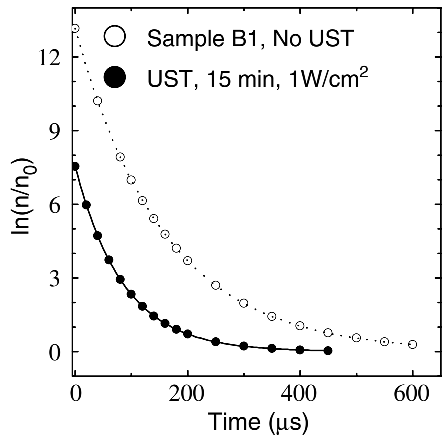

Figure 3. Decay transient of $\ln(n/n_0)$ before (open symbols) and after (filled symbols) UST for the sample B1. Fitted curves have been plotted as dotted (before UST) and continuous (after UST) lines.

One can find it by substituting equation (3) into (2). This result shows that upon an exponential decrease in $V_{oc}(t)$, the carrier concentration can decrease following

$$n = n_0 \times \exp\left(\frac{qV_{oc}(0)}{\beta kT} \times \exp\left(-\frac{t}{\tau_0}\right)\right). \tag{6}$$

The analysis shows that distinct from equation (5), the power of the exponential function in equation (6) contains another exponential function with the characteristic lifetime τ_0. This result indicates that even a small variation of τ_0 can cause a drastic change in the carrier concentration and other electrical parameters of the DE p–n junction. Since commonly the characteristic carrier lifetime τ_0 can be sensitive to the variation of external perturbations such as temperature and pressure, electrical parameters of the DE Si p–n junction are expected to be strongly sensitive to small variations of the external perturbations. The reason for the exponential decay of $V_{oc}(t)$ should not be ascribed to DE. A more detailed study is needed to clarify the reason. At the current stage of understanding the safest way is to state the possibility of exponential decay of $V_{oc}(t)$ in DE Si.

3.2. *Non-equilibrium carrier concentration and lifetime*

By decomposing the exponential function in equation (6) into the Taylor series one can find that

$$\exp\left(-\frac{t}{\tau_0}\right) \approx 1 - \frac{t}{\tau_0} + \cdots, \tag{7}$$

which is valid in the time range $0 \leqslant t \leqslant \tau_0$. Then equation (6) can be rewritten as

$$\begin{aligned} n &\approx n_0 \times \exp\left(\frac{qV_{oc}(0)}{\beta kT} \times \left(1 - \frac{t}{\tau_0}\right)\right) \\ &\approx n_0 \times \exp\left(\frac{qV_{oc}(0)}{\beta kT}\right) \times \exp\left(-\frac{t}{\tau_0}\right). \end{aligned} \tag{8}$$

Comparing equation (8) with equation (5) one can find that τ_0 can be regarded as the carrier lifetime. The fact that τ_0 is in

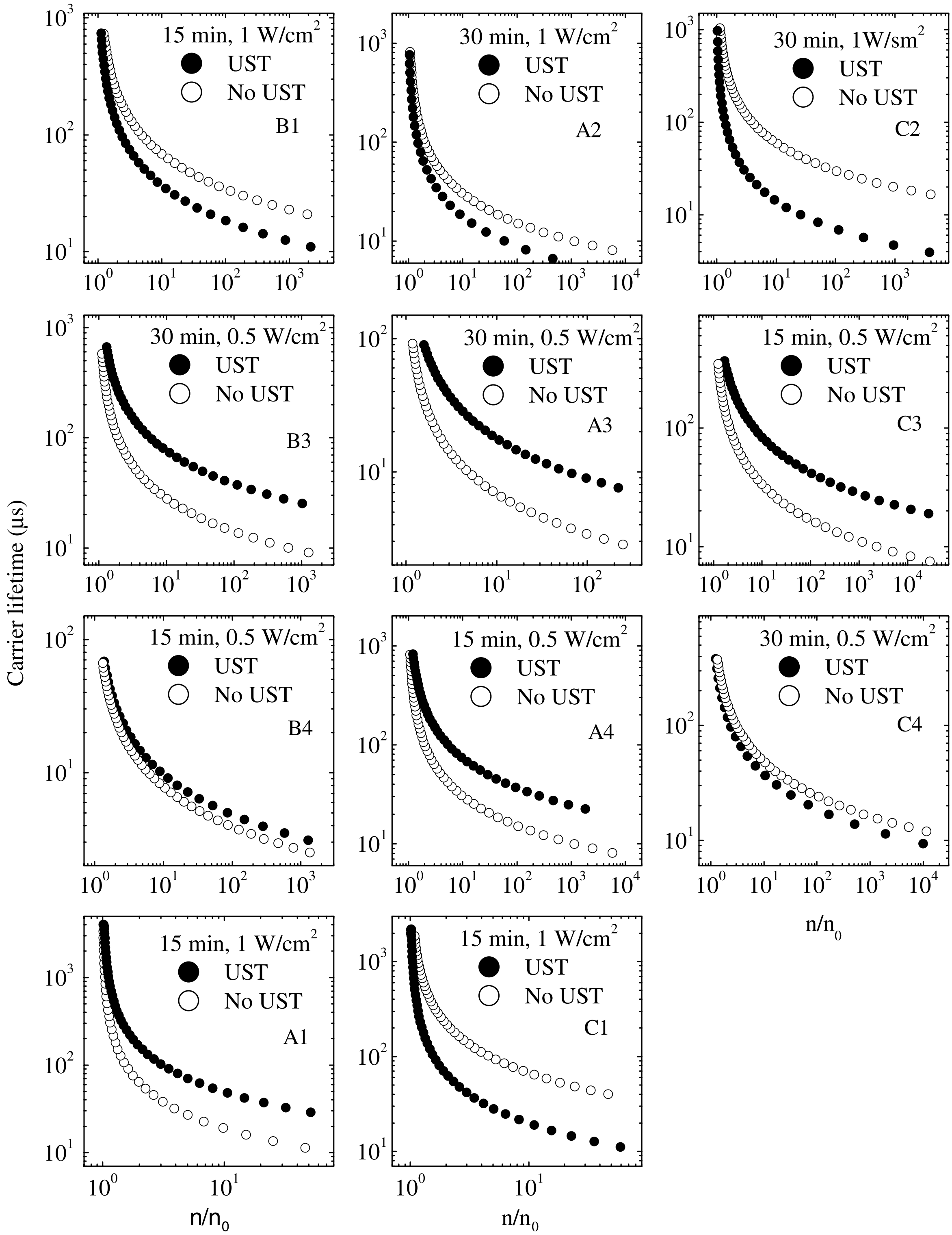

Figure 4. Dependence of the carrier lifetime on excess carrier concentration before (○) and after (●) UST. The labels A1–C4 denote the samples listed in table 1.

the power of the second exponential function of equation (6) shows that τ in equation (5) is not constant. It varies with time t because of variation of the carrier concentration. To demonstrate this we have studied the transience of the carrier concentration upon switching the illumination off. Knowing the experimentally measured time dependence of the open-circuit voltage $V_{oc}(t)$, we have calculated by equation (2) the relation n/n_0 at different times t. Then the dependence of $\ln(n/n_0)$ on time t has been plotted for the cases before and after the UST. The results are presented in figure 3 for sample B1. The experimental data have been nicely fitted with the single exponential function. Ln (n/n_0) exponentially decreases with time t. This result confirms the validity of the suggestion that the carrier concentration decreases according

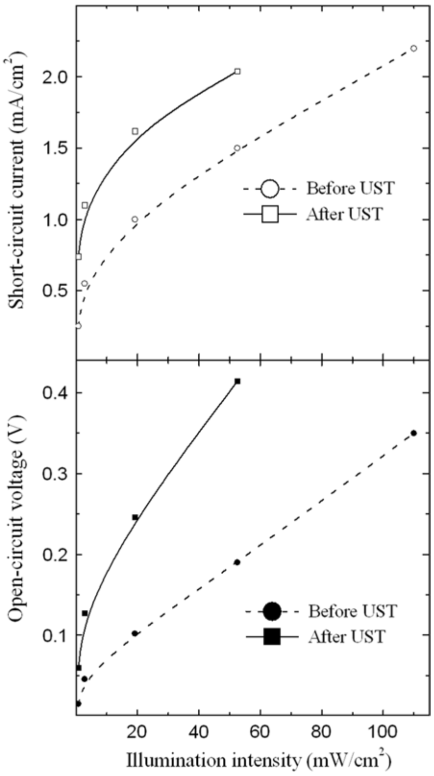

Figure 5. Dependence of the short-circuit current J_{sc} and the open-circuit voltage V_{oc} on the intensity of illumination Φ of the sample A4 before and after UST within 30 min at a frequency of 2.4 MHz and power of 0.5 W cm^{-2}.

to equation (6). Consequently, n/n_0 decreases faster than according to the single exponential function of equation (5).

Below we demonstrate that the carrier lifetime τ (1) is not constant and it depends on the carrier concentration n/n_0. To this end we have interpolated the time dependence of n/n_0 (figure 3) and calculated its first derivative. Modifying equation (1)

$$\frac{\mathrm{d}(n/n_0)}{\mathrm{d}t} = -\frac{n/n_0 - 1}{\tau} \qquad (9)$$

and knowing $\mathrm{d}(n/n_0)/\mathrm{d}t$ and n/n_0 at different times t, we calculated τ for different values of t from equation (9). The thus calculated carrier lifetime has been plotted as a function of the relation n/n_0. The results are presented in figure 4. It is seen that the carrier lifetime is not constant. It is very sensitive to the variation of the excess carrier concentration and decreases drastically with increasing n/n_0, thus confirming the above-mentioned sensitivity of the dislocation engineered Si p–n junction to variations of the illumination intensity.

It is interesting to note that at low concentrations of non-equilibrium free carriers ($n/n_0 < 1$), carrier lifetimes before and after UST are almost the same. As $n/n_0 \approx 1$ the carrier lifetime steeply decreases with increasing carrier concentration. At larger concentrations of carriers $n/n_0 > 1$ the lifetimes before and after UST considerably differ each from other, because of the ultrasound-induced modulation of the defect spectra. This result indicates that the electrical parameters of the DE p–n junction are controlled by deep level defects, which undergo ultrasound-induced transformations.

Figure 5 presents the dependence of the short-circuit current J_{sc} and the open-circuit voltage V_{oc} of the DE Si on the intensity of illumination Φ before and after UST within 30 min at the frequency of 2.4 MHz and power of 0.5 W cm^{-2}. It is seen that both J_{sc} and V_{oc} steeply increase with increasing Φ at low illumination intensities and more slowly increase at larger values of Φ. This result is in good agreement with the above finding as regards the carrier concentration dependence of the lifetime (figure 4). At small illumination intensities Φ the carrier diffusion length L steeply decreases with Φ, because of the steep decrease in τ (figure 4), but still remains larger than the base thickness w. However, at larger Φ, the magnitude of L becomes considerable closer to w. Furthermore, the decrease in τ (figure 4) and, respectively, L with increasing Φ takes place more slowly. This might cause a slower increase in J_{sc} and V_{oc} with increasing Φ.

It should be noted that both J_{sc} and V_{oc} before UST are smaller than those after UST thus demonstrating UST-induced enhancement of the electrical parameters of the DE Si. This result correlates well with the UST-stimulated increase in the carrier lifetime displayed in figure 4 for the sample A4.

4. Conclusion

Thus, an open-circuit voltage decay transient has been studied in the dislocation-engineered Si p–n junction. It is found that upon switching off the illumination, the open-circuit voltage decreases with time according to the single exponential function. This dependence is found to correspond to the fast decrease in the carrier concentration with time according to two exponential functions one of which is built into the power of the other. This dependence can be the reason for the high sensitivity of the dislocation-engineered Si p–n junction to band-to-band illumination intensity. The carrier lifetime is estimated and found to depend on the carrier concentration. The UST of the samples has been performed. It is shown that the open-circuit voltage of the dislocation-engineered Si decreases because of the decrease in the carrier concentration. From the lifetime studies the latter is shown to be because of ultrasound-induced modulation of the defect spectra. We have demonstrated in this paper that the dislocation-engineered Si can be used not only as a light-emitting diode but also as a receiver.

Acknowledgments

This work has received financial support from the Academy of Sciences of Uzbekistan and the Research Council of Norway through the NANOMAT project. The authors thank Dr B Aytbaev and Kh Ismailov for assistance in measurements and Professor S Kh Shamirzaev, R A Muminov and I Atabaev for supporting the work. The authors also wish to thank Dr M Lourenco and Professor K Homewood (Advanced Technology Institute, School of Electronics and Physical Sciences, University of Surrey, Guildford, Surrey GU2 7XH, UK) for providing the samples of the dislocation-engineered silicon.

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