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Dependence of minority charge carriers lifetime on point defects type and their concentration in single-crystal silicon

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Using the computer simulation method it was studied the dependences of nonequilibrium electrons lifetime from concentration of elementary bulk point defects and various complexes of the bulk point defects, which may be present in the n^+-p-p^+ diode structures based on p-type conductivity boron doped silicon crystals with 10 Ohm·cm resistivity, grown by the Czochralski method. A number of obtained results well correlated with the experimental data related to the effects of photon degradation in solar cells which based on considered type silicon crystals (Si–SC) and influence of a stationary magnetic field on such devices efficiency. Overall, our results provide additional possibility for the evolution features prediction of electronic, and consequently, functional parameters, not only for Si-SC, but also for other devices based on such diode structures. It will allow looking for the most efficient and cost effective ways to optimize their design-technological solutions, and also estimates their reliability and durability level.

Методом компьютерного моделирования исследованы зависимости времени жизни неравновесных электронов от концентрации элементарных объемных точечных дефектов и различных комплексов объемных точечных дефектов, которые могут присутствовать в n^+-p-p^+ диодных структурах на основе кристаллов кремния p-типа проводимости с удельным сопротивлением 10 Ом·см, выращиваемых методом Чохральского и легируемых бором. Ряд полученных результатов согласуется с известными экспериментальными данными о влиянии солнечного излучения и стационарного магнитного поля на эффективность работы кремниевых фотоэлектрических преобразователей (Si-ФЭП) с диодными структурами рассматриваемого и подобного типа. Результаты настоящей работы обеспечивают дополнительную возможность прогнозирования особенностей эволюции электронных, а следовательно, и функциональных параметров, не только Si-ФЭП, но и других приборов на основе таких диодных структур, что позволит наиболее эффективно и экономически выгодно искать пути оптимизации их конструктивно-технологического решения, а также оценивать уровень их надежности и долговечности.

1. Introduction

Rapid development of ecologically clean technologies for energy supplying and impressive practical achievements in photovoltaic have caused the irreversible avalanche-like growth of world solar cells (SC) production [1, 2]. Recently, about 90 % of the total world solar cells manufacturing is their serial production on the silicon base, from which up to 30 % is belong to single-crystal Si-SC [2]. According to [1] the mentioned tendency will occur in the nearest and more distant prospects. This caused an actuality of research aimed at single-crystal Si-SC cost reduction and their efficiency increase.

Currently, such research includes a computer simulation of electronic processes which conditioned Si-SC efficiency level depending on the features of their design and technological solutions (DTS) and acting external factors (EF). The mentioned above information directly applies to the single-crystal Si-SC, the efficiency of which depends essentially from quality of their base crystals (Si-BC) after production, storage and operation.

In turn, the quality of Si-BC, determined by the single-crystal silicon defectiveness character and degree, significantly affects on one of the key Si-SC electronic parameters — minority charge carriers (MCC) lifetime τ. In the case of dominant role of bulk point defects (BPD) and their complexes (CBPD), as recombination centers (RC), the MCC lifetime decreases with RC concentration N_t growth, that leads to efficiency reduction of considered devices [3]. Note that according to appropriate comprehensive literary data among the most effective RC in the Si-BC are following BPD: vacancies V, interstitial chromium Cr_i, titan Ti_i, zinc Zn_i, gold Au_i, molybdenum Mo_i, iron Fe_i, and also CBPD: bivacancies V_2, trivacancies V_3, V–P, V–2As, Ti_i–Ti_i, Zn_i–Zn_i, V_2–O_i, Cr_i–B, Fe_i–B, Fe_i–Al, B_i–O_i and C_i–O_i, where O_i — interstitial oxygen, and atoms of chemical elements without subscripts correspond to substitutional impurity in the silicon lattice.

Under the influence of EF in the BPD and CBPD ensemble inside Si-BC the reconstructions may occur. In some cases, for example, under the influence of intense solar radiation, they result in to N_t increase (owing to the photochemical generation Fe_i–B and B_i–O_i complexes), and hence to τ and Si-SC efficiency decrease [4]. In other cases, for example, under the influence of a stationary magnetic field (SMF) the N_t level is reduced, which results in to τ and Si-SC efficiency increase [5]. At that it still remains as open the problem about the specifics of the reconstruction in point defects ensemble inside Si-BC under the SMF influence on Si-SC. At the same time, the solution of this problem would be essentially facilitated by establishing a correlation between the experimentally registered τ changes and mathematically modeled τ from N_t dependencies for different BPD and CBPD. Furthermore, the decision of emphasized problem is acquired at the present time a special actuality in connection with the start of applied research on the development of next-generation photovoltaic module based on multi-junction single crystal Si-SC with n^+-p-p^+-type vertical diode meshes. The module efficiency of such Si-SC can be increased about in 1.1 times (up to 26 % in a highly concentrated solar radiation) at the expense of influence on Si-SC the homogeneous SMF of about 0.5 T induction [6]. Naturally, the results of computer simulation of intrinsic point defects, various impurities and also their complexes influence on τ in Si-BC will provide additional ability to predict the evolution of electronic and, therefore, functional parameters, not only Si-SC, but also other devices based on single-crystal silicon. This will allow looking for ways to optimize their DTS most efficiently and cost effectively, as well as to estimate their reliability and durability level.

In connection with the information mentioned above a purpose of the research, which main results are described below, was to create a mathematical model of Si-BC p-type conductivity with submicron thickness diffusion n^+- and p^+-layers under the opposite planar surfaces, and also subsequent analytical research of the MCC — electrons lifetime τ_n in such base crystals p-layer dependence from range and concentration of the most probable BPD and CBPD in Si-BC.

2. Experimental

In current research work it was created a mathematical model for the above mentioned Si-BC with 200–300 μm thickness from silicon SHB-10 mark, grown by the Czochralski method. The model provides a possibility of existence in Si-BC p-layer earlier mentioned BPD and CBPD. At that the existence of P, As, and Al atoms with concentrations less than 10^{14} cm^{-3} in the boundary of n^+- and p^+-layers with p-type silicon SHB-10 mark of boron doped with concentration about $1.35\cdot10^{15}$ cm^{-3}, allowed under the peculiarities of thermodiffusion method used for n^+-p-p^+ diode structure forming. Interstitial atoms of carbon and oxygen are well-known attribute of single-crystal silicon grown by Czochralski method. The atoms of other chemical elements are classified as background impurities which are well known for such silicon.

Creating the mathematical model of the investigated objects was carried out by using a specialized electronic spreadsheet for computer simulation of Si-SC and also

for analytical study of problems related to real Si-BC electronic parameters influence on the Si-SC output parameters (finally — on the efficiency of such devices) [7, 8].

The calculation of τ_n values in the investigated objects was performed at 300 K. In the Table below the values of recombination parameters are presented: electrons and holes capture cross-section area $\sigma_{n,p}$, and also the depth of recombination centers E_c-E_t levels in the silicon band gap towards conduction band bottom — harmful for considered diode structures BPD and CBPD which taken into account in this research.

3. Results and discussion

Dependences of τ_n from N_t for BPD and CBPD specified in the Table were calculated and plotted in Fig. 1 using the created mathematical model.

As it seems from the graphs presented in Fig. 1, a obtained dependences of τ_n from CBPD–V–P, V–2As, V_2, V_2–O_i and V_3 concentration, are grouped in accordance with the amount of vacancies, contained in CBPD: CBPD with one (V–P and V–2As), two (V_2 and V_2–O_i) and three (V_3) vacancies. Graphs of τ_n–N_t dependences for V–P and V–2As complexes practically do not differ from each other, and the effect of such CBPD on the τ_n value could be described by a single averaged curve. Qualitatively similar situation take place in case of V_2 and V_2–O_i CBPD which, however, have a negative influence on the τ_n value versus CBPD which based on the one vacancy. However, as it seems from Fig. 1,a the complexes formed by three vacancies effect the most negatively on τ_n value. The above stated enable to conclude that the degree of negative impact of CBPD with vacancies on the τ_n value at N_t = const is determined by the number of vacancies, which enters into a CBPD composition. The negative impact significantly increases with vacancies number growth. Therefore, owing to the fact that for single-crystal the integration of monovacancies in bivacancies and trivacancies and also these defects in more intricate complexes is energetically profitably, it should be expected that after manufacturing the device structure based on considered type Si-BC with time in it may occurred a τ_n value decrease under the influence of EF, providing the necessary level of diffusion mobility for corresponding structural units in real silicon crystal.

Table. Recombination parameters of harmful for Si-SC bulk point defects (BPD) and their complexes (CBPD) that were used at the calculation of τ_n (N_t) dependences

BPD and CBPD	E_c-E_t, eV	σ_n, cm^2	σ_p, cm^2	References
Ti_i	0.270	$3.1\cdot10^{-14}$	$1.4\cdot10^{-15}$	[7]
Ti_i–Ti_i	0.865	$1.3\cdot10^{-14}$	$2.8\cdot10^{-17}$	
Zn_ii	0.795	$1.5\cdot10^{-15}$	$4.4\cdot10^{-15}$	
Zn_i–Zn_i	0.470	$1.3\cdot10^{-19}$	$6.6\cdot10^{-15}$	
Cr_i	0.240	$2.0\cdot10^{-14}$	$4.0\cdot10^{-15}$	[7, 9, 10]
Cr_i–B	0.844	$5.0\cdot10^{-15}$	$1.0\cdot10^{-14}$	
Fe_i	0.745	$4.0\cdot10^{-14}$	$7.0\cdot10^{-17}$	[7, 11]
Fe_i–B	0.260	$5.0\cdot10^{-15}$	$3.0\cdot10^{-15}$	
Fe_i–Al	0.924	$1.0\cdot10^{-15}$	$2.0\cdot10^{-14}$	[9]
Au_i	0.550	$1.4\cdot10^{-16}$	$7.6\cdot10^{-15}$	[7]
Mo_i	0.845	$8.0\cdot10^{-15}$	$6.0\cdot10^{-16}$	
C_i–O_i	0.764	$2.5\cdot10^{-14}$	$2.5\cdot10^{-15}$	[12, 13]
V–P	0.847	$5.0\cdot10^{-16}$	$5.0\cdot10^{-16}$	
V–2As	0.924	$2.5\cdot10^{-15}$	$2.5\cdot10^{-15}$	
V_2	0.420	$2.0\cdot10^{-15}$	$2.0\cdot10^{-15}$	
V_2–O_i	0.545	$1.7\cdot10^{-15}$	$9.0\cdot10^{-14}$	
V_3	0.460	$5.0\cdot10^{-15}$	$5.0\cdot10^{-14}$	

The comparative analysis of τ_n from N_t dependences, presented in Fig. 1,b enable to conclude that interstitial titanium and zinc atoms at concentrations above 10^{10} cm^{-3} start to affect negatively on τ_n value, while CBPD from pair of such identical atoms start to affect negatively on the specified parameter at much higher concentrations which are 10^{12} cm^{-3} and 10^{15} cm^{-3} for Ti_i–Ti_i and Zn_i–Zn_i, respectively. Such circumstance may be stipulated by the following. Owing to formation the CBPD from two interstitial atoms of titanium or zinc, a saturation of dangling metal bonds of these point defects occur, that properly from the Table leads to a decrease $\sigma_{n,p}$ values from 10^{-14}–10^{-15} cm^2 for Ti_i and Zn_i atoms up to 10^{-17}–10^{-19} cm^2 for CBPD Ti_i–Ti_i and Zn_i–Zn_i. In turn, the $\sigma_{n,p}$ reduction causes the decrease of Ti_i–Ti_i and Zn_i–Zn_i complexes negative influence on τ_n. Thus, the improvement of MCC electronic parameters in the silicon crystals in the presence of Ti_i and Zn_i impurities can be achieved by carrying out a treatment that will lead to the integration of individual titanium and zinc interstitial

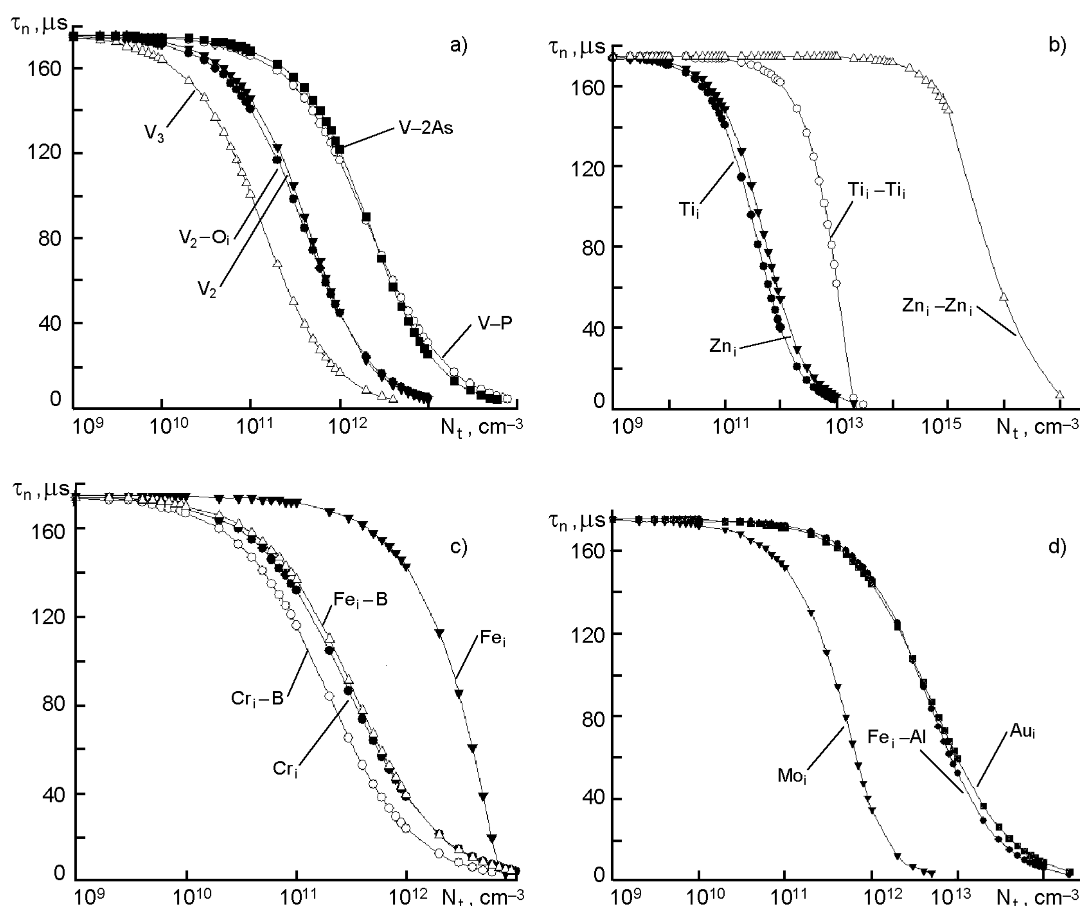

Fig. 1. Dependences of nonequilibrium electrons lifetime from point defects and their complexes concentration in the p-layer of n^+-p-p^+-type diode structure based on SHB-10 mark of Si-BC, grown by the Czochralski method (graphs on the a–d fragments are named in accordance with BPD and CBPD types by the presence of which they are conditioned).

atoms in the binary complexes from identical atoms.

Since the real Si-BC of considered type usually is characterized by the presence of more than one type of harmful CBPD, the possibility of several CBPD types influence on MCC electronic parameters accounting is practically interested. So the next stage of this research was the modeling of the simultaneous influence of two different types of harmful CBPD or CBPD and BPD on τ_n value.

As mentioned earlier, one of the main harmful impurity, which is always present in silicon crystals grown by the Czochralski method is the interstitial oxygen. Therefore, for the considered type Si-BC the B_i–O_i complex examined as the permanently present kind of CBPD. In addition to O_i for such Si–BC as typical impurities also are C_i and Fe_i. Therefore, at the calculations on the second stage of the research in addition to the B_i–O_i complex, taken into account the following CBPD and BPD: V_2, V_2–O_i, Fe_i–B, C_i–O_i and Fe_i — to study the influence on τ_n value each of them in pair with B_i–O_i. The calculated diagrams of τ_n values distribution depending on the various pairs from specified CBPD and BPD concentrations presented on Fig. 2 and Fig. 3.

All of these diagrams clearly indicate on the possibility of significant enhancement of early mentioned photon degradation effect in Si-SC based on Si-BC which grown by Czochralski method and doped by boron at the generation in them under the influence of solar radiation, together with B_i–O_i complexes on many orders lower concentrations of bivacancies and V_2–O_i, Fe_i–B and C_i–O_i complexes. At the same time it is very interesting the fact of increasing the interstitial iron atoms negative contribution after their introduction in complexes with interstitial atoms of the main dopant — boron, that follows from a comparison of the diagrams presented in fragments a and b of the

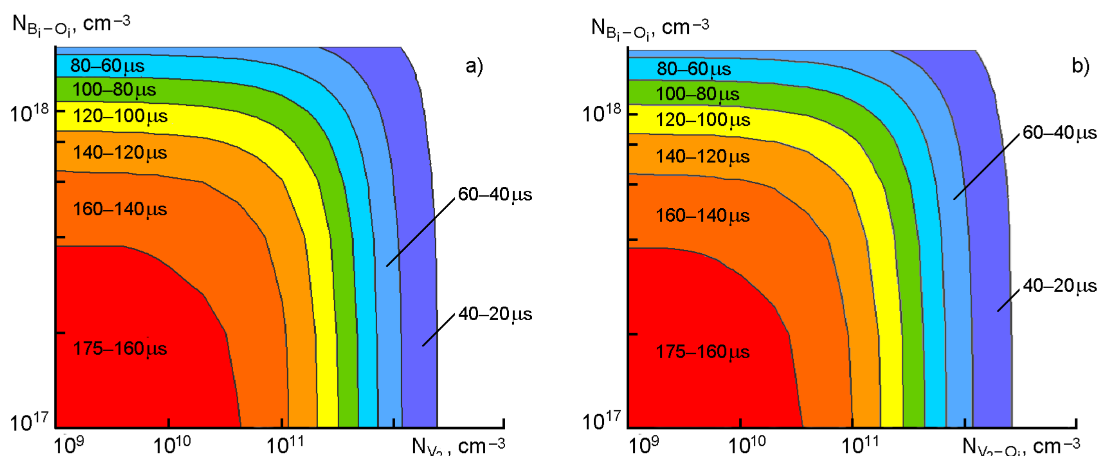

Fig. 2. Diagrams of $\tau_n(N_t)$ dependences for Si-BC considered type at simultaneously dominating influence of: *a* — B_i–O_i complexes and bivacancies; *b* — B_i–O_i and V_2–O_i complexes (numeric values in the diagram field indicate the τ_n range at corresponding concentrations of BPD and CBPD).

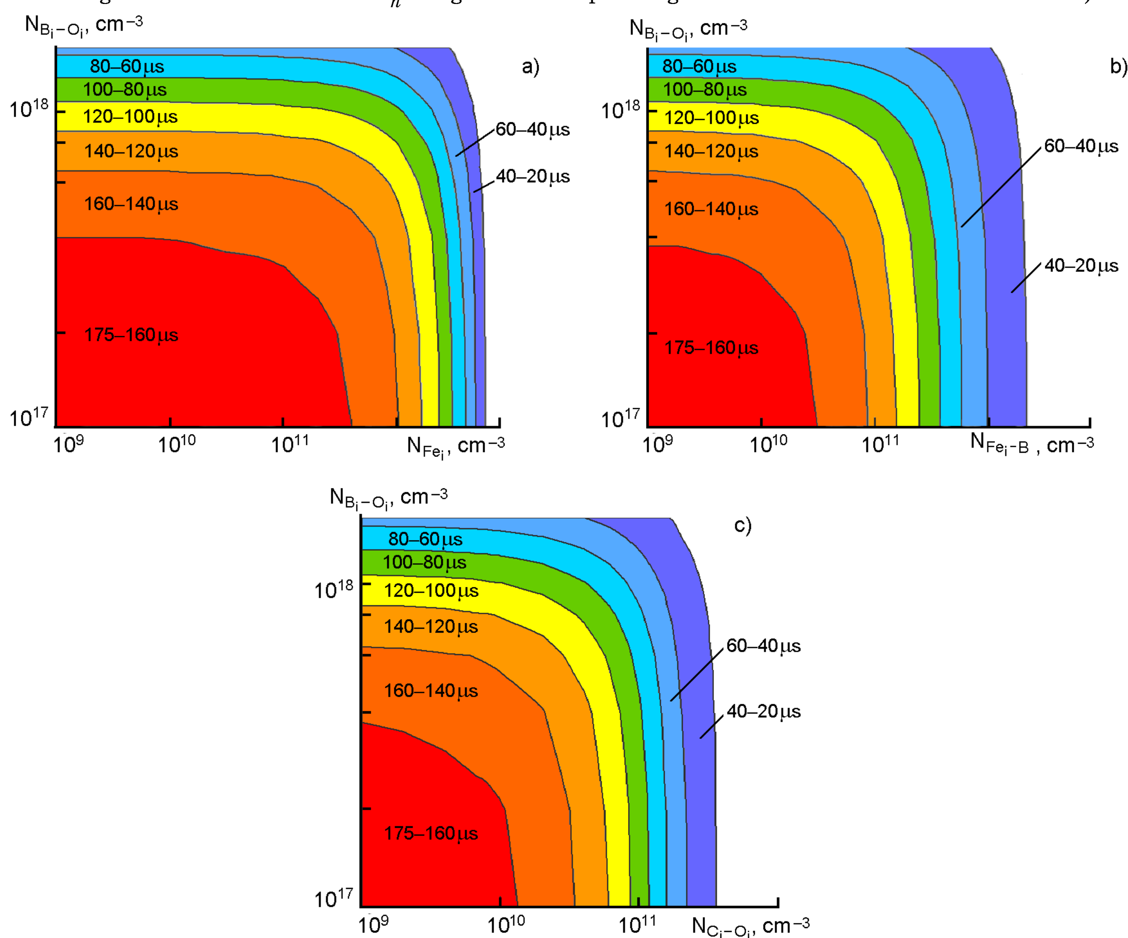

Fig. 3. Diagrams of $\tau_n(N_t)$ dependences for Si-BC considered type at simultaneously dominating influence of: *a* — B_i–O_i complexes and iron interstitial atoms; *b* — B_i–O_i and Fe_i–B complexes; *c* — B_i–O_i and C_i–O_i complexes (numeric values in the diagram field indicate the τ_n range at corresponding concentrations of BPD and CBPD).

Fig. 3. Note that in [4] the emphasized effect is described as experimentally registered fact. At that, diagrams, presented in Fig. 3, *c* shows that maximum enhancement of photon degradation effect in Si-SC, based on the considered Si-BC, should be expected

in the case of C_i–O_i complexes small concentration additives to available in incomparably larger concentrations B_i–O_i complexes.

In addition, our results shown in Fig. 2, b, may serve as a starting point for further development of physical conceptions concerning the nature of the noted in introduction beneficial influence of a stationary magnetic field on efficiency of the Si-SC with considered type Si-BC. Indeed, as it can be seen from Fig. 2, b, a slight decrease of V_2–O_i complexes concentration in Si-BC causes appreciable increase of τ_n, which is a serious prerequisite for Si-SC efficiency growth. On the other hand, in [5] it was proposed the hypothesis, initiated by ideas from [14] about the involvement in the effect of Si-SC efficiency increase under the SMF influence the decomposition process of CBPD consisting from silicon atoms vacancies and interstitial oxygen atoms. So now the obvious argument in favor of this hypothesis validity is obtained. After this, the further study of SMF influence physics on τ_n values and Si-SC efficiency with n^+-p-p^+-type diode structure may be developed at realization of appropriate comprehensive analysis. For example, using methods of deep level transient spectroscopy (DLTS) [15] in conjunction with studies of the MCC lifetime in Si-BC [3] and Si-SC output parameters determination [16] before and after the SMF action in combination with computer simulations of τ_n dependencies from point defects structure reconstruction results in Si-SC n^+-p-p^+ diode structure under the SMF influence.

4. Conclusions

A mathematical model of solar cells base crystals with p-type conductivity, and 200–300 μm thickness from SHB-10 mark silicon, grown by the Czochralski method, with submicron thickness n^+- and p^+-diffusion layers under the opposite planar surfaces has been developed. The computer simulations of electrons lifetime τ_n dependences from assortment and concentration N_t of the most probable bulk point defects and their complexes in such base crystals p-layer were carried out by using of this model. It has been shown that degree of CBPD with vacancies V negative impact on τ_n value at N_t = const determined by the quantity of vacancies, which enters into a CBPD composition and significantly increase with the transition from monovacancies to bivacancies V_2 and trivacancies V_3. In contrast, the pairing of individual titanium or zinc interstitial atoms results in significant τ_n increase. It has been detected the extremely strong influence of BPD and CBPD: V_2, V_2–O_i, Fe_i–B, C_i–O_i and Fe_i small concentrations on τ_n value which in the presence of significantly higher B_i–O_i complexes concentrations perceptibly decreases with N_t increasing for each defect from above listed. At the same time C_i–O_i complexes rendered record strong influence on τ_n value. A number of obtained results well correlated with the experimental data which relate to the effects of photon degradation in solar cells based on considered type silicon crystals as well as to influence of a stationary magnetic field on such devices efficiency. Overall, our results provide additional possibility for the evolution features prediction of electronic, and consequently, functional parameters, not only for Si-SC, but also for other devices based on such diode structures. It will allow looking for most efficient and cost effective ways to optimize their design-technological solutions, and also estimates their reliability and durability level.

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References

1. E.Despotou, A.E.Gammal, B.Fontaine et al., Global Market Outlook for Photovoltaics Until 2014; European Photovoltaic Industry Assosiation (EPIA), Renewable Energy House, Brussels, Belgium, 15 May 2010. http://www.epia.org/fileadmin/EPIA_docs/public/Global_Market_Outlook_for_Photovoltaics_until_2014.pdf.
2. W.Hoffmann, L.Waldmann, in: High-efficient Low-cost Photovoltaics. Recent Developments, ed. by V.Petrova-Koch, R.Hezel and A.Goetzberger, Springer-Verlag, Berlin Heidelberg (2009).
3. A.L.Fahrenbruch, R.H.Bube, Fundamentals of Solar Cells. Photovoltaic Solar Energy Conversion, Academic Press, New York (1983).
4. J.Schmidt, K.Bothe, D.Macdonald et al., Electronically Stimulated Degradation of Silicon Solar Cells (2005); http://ssc.cecs.anu.edu.au/files/Paper_MRS2005_final.pdf.
5. R.V.Zaitsev, V.R.Kopach, M.V.Kirichenko et al., *Functional Materials*, **17**, 554 (2010).
6. E.Sokol, V.Kopach, R.Zaitsev et al., *Vidnovlyuvalna Energetyka (Renewable Energetics)*, **2**, 18 (2011).

7. A.Cuevas, R.Sinton, QSS model — Excel Spreadsheet for Simulating QSSPC Lifetime Measurements (2010); http://ssc.cecs.anu.edu.au/files/QSSModel9Nov2010.xls.
8. A.Cuevas, R.Sinton, τ-model: a Spreadsheet for Modeling the Quasi-steady-state Effective Lifetime (2006); http://ssc.cecs.anu.edu.au/files/TauModelmanualshort.pdf.
9. S.Indradeep, Correlation of Grain-to-grain Electrical Properties with Impurities and Defects in Solar Grade Polycrystalline Silicon, Ph.D. Thesis, North Carolina (2002); http://www.lib.ncsu.edu/theses/available/etd-08062002-133426/unrestricted/-etd.pdf.
10. A.Chantre, *J.Phys. Arch.*, **44**, 269 (1983).
11. B.B.Paudyal, K.R.McIntosh, D.H.Macdonald, G.Coletti, in: Proc. of the 24th Eur. Conf. on Photovoltaic Solar Energy Conversion, Hamburg, Germany (2009), p.981.
12. C.J.Bebek, D.E.Groom, S.E.Holland et al., Proton Radiation Damage in High-resistivity *n*-type Silicon CCDs (2001); http://escholarship.org/uc/item/7gh2k9vg.
13. P.T.Neuvonen, Effects of Vacancy-type Defects in Silicon Based Particle Detectors: Master's Thesis, Lappeenranta University of Technology (2008); http://www.doria.fi/bitstream/handle/10024/38649/Finished.pdf?sequence=1.
14. V.A.Makara, L.P.Steblenko, A.M.Kuryliuk et al., *Functional Materials*, **16**, 237 (2009).
15. D.V.Lang, *J. Appl. Phys.*, **45**, 3023 (1974).
16. K.Emery, in: Handbook of Photovoltaic Science and Engineering, ed. by A.Luque and S.Hegedus, John Wiley & Sons, Ltd., Chichester (2003), p.701.

Залежність часу життя неосновних носіїв заряду від типу та концентрації точкових дефектів у монокристалічному кремнії

Р.В.Зайцев, В.Р.Копач, М.В.Кіріченко, Г.М.Дорошенко, Г.С.Хрипунов

Методом комп'ютерного моделювання досліджено залежності часу життя нерівноважних електронів від концентрації елементарних об'ємних точкових дефектів і різноманітних комплексів об'ємних точкових дефектів, які можуть бути присутніми в n^+-p-p^+ діодних структурах на основі кристалів кремнію p-типу провідності з питомим опором 10 Ом·см, котрі вирощуються методом Чохральського і легуються бором. Ряд отриманих результатів узгоджується з відомими експериментальними даними щодо впливу сонячного випромінювання і стаціонарного магнітного поля на ефективність роботи кремнієвих фотоелектричних перетворювачів (Si-ФЕП) з діодними структурами розглянутого і подібного типу. Загалом, результати цієї роботи забезпечують додаткову можливість прогнозування особливостей еволюції електронних, а тому і функціональних параметрів, не тільки Si-ФЕП, але й інших приладів на основі таких діодних структур, що дозволить найбільш ефективно і економічно вигідно шукати шляхи оптимізації їх конструктивно-технологічного рішення, а також оцінювати рівень їх надійності та довговічності.