

The mechanisms of the influence of  $\gamma$ -irradiation with the doses up to  $10^8$  rad on the recombination and photoenergetic parameters of solar cells (SCs) fabricated on the basis of single- and multicrystalline silicon and uncovered or covered with a diamond-like carbon film (DLCF) have been studied. The efficiency of SCs covered with a thin antireflection DLCF and subjected to  $\gamma$ -radiation has been demonstrated to degrade to a less extent in comparison with that of SCs without the DLCF. In the case of  $\gamma$ -irradiation of SCs, which are based on multi-crystalline silicon, to the exposure doses  $D \leq 10^6$  rad, the gettering of recombination-active impurities located in the bulk of SCs by grain boundaries has been found.

#### 1. Introduction

A large attention, which is drawn to the researches of radiation-induced defects in semiconductors, is stimulated by the high sensitivity of semiconductor properties to the influence of radiation treatment, as well as by the wide application of semiconductor-based devices under such conditions which imply the existence of radiation of various types (in outer space, at nuclear power plants, accelerators of elementary particles, etc). In particular, the enhancement of radiation resistance of silicon-based SCs is one of the challenging problems of modern solar power engineering in the field of spacecraft designing.

It is known that, under the action of high-energy irradiation and owing to the violation of the natural periodicity of the semiconductor's lattice, there emerge defects in the form of vacancies, interstitial atoms, and complexes of displaced atoms, some portion of which recombine, while the rest, due to their interaction with one another, as well as with impurities and other irregularities of the crystal structure, forms stable complexes; all that results in a change of the electric characteristics of semiconductors [1–4]. In particular, those stable complexes are the effective centers of recombination and lead to a reduction of the lifetime of nonequilibrium charge carriers, which is a critical parameter that governs the efficiency of silicon-based SCs. Nowadays, the influence of ionizing electron, proton, or neutron irradiation on the photo-electric characteristics of silicon-based SCs is studied rather thoroughly (see, e.g., works [3–5]).

Unlike the corpuscular irradiation, in the case of  $\gamma$ irradiation, defects are formed owing to the Compton effect, when  $\gamma$ -rays produce high-energy electrons in a semiconductor, which are capable to displace atoms from their places in the crystal lattice when colliding with them elastically [3]. Under the action of  $\gamma$ -quanta, radiation-induced defects appear in the silicon's volume, being uniformly distributed over the crystal depth. The defects emerge in the form of A-, E-, and K-centers, the concentration of which monotonously increases with the growth of the irradiation dose [1–3, 7]. Among the important factors that affect the radiation resistance of silicon, there are the initial concentrations of defects and impurities, as well as the type of semiconductor conductivity.

In Si of the *p*-type, which is mainly used for fabricating SCs, dominant are *K*-centers of recombination [1–3]. The kinetics of their formation, as well as the kinetics of the formation of *A*- and *E*-centers and divacancies, is affected by the drains (getters) of various origins, in particular, structural defects, interfaces, and so on [8].

Therefore, the aims of this work were (i) to study and compare the mechanisms of influence of various exposure doses of  $\gamma$ -radiation on the SCs fabricated on the basis of either single- or multi-crystallite (polycrystalline) silicon (the latter is structurally less perfect and contains numerous interfaces), (ii) to study the influence of antireflection coatings prepared on the basis of amorphous carbon films and possessing various optical characteristics on the radiation stability of such SCs, and (iii) to study the regimes of thermal annealing

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which can provide the maximal recovery of the photoelectric characteristics of SCs subjected to  $\gamma$ -radiation.

# 2. Specimen Preparation and Experimental Method

Solar cell specimens for investigations were fabricated on the basis of either single- or multi-crystallite p-silicon, according to the technological routine which included the following stages:

(i) diffusion of the doping impurity (phosphorus) from a  $POCl_3$  source in order to create an emitter  $n^+$ -layer;

(ii) formation of the front contacts: (a) for SC specimens on the basis of multi-crystallite silicon (multi-Si), the front contacts were created by the screen printing method and using a paste which contained Ag; (b) for SC specimens on the basis of monocrystalline silicon (mono-Si), the front contacts were produced photolithographically on Al;

(iii) formation of the Al back contacts; this stage was followed by thermal annealing of the specimens, which ensured the creation of an isotypic  $p - p^+$ -junction.

Some of SC specimens fabricated on the basis of mono- or multi-Si had an antireflection a-C:H:N diamond-like coating. The DLCFs were deposited onto finished SCs using the PE-CVD method (at 13.56 MHz) from a mixture of  $H_2:N_2:CH_4:Ar = 10:4:3:1$ , at a discharge power of 150 W, and at the 0.8-Torr pressure in the reactor.

Some of the fabricated specimens were irradiated by  $\gamma$ -quanta from a Co<sup>60</sup> source to the exposure doses of 10<sup>5</sup>, 10<sup>6</sup>, 5 × 10<sup>6</sup>, 10<sup>7</sup>, 5 × 10<sup>7</sup>, and 10<sup>8</sup> rad, while the others served as the reference ones. Heat treatments of the specimens were executed at temperatures T = 250 and 400 °C during 15 min.

The specimens were applied to study the spectral dependences of the short circuit photocurrent and the light current-voltage load characteristics (LCVLCs). For this purpose, a test station for phototechnical testing of SCs [9–11] certified by the State Committee of Ukraine on Technical Regulation and Consumer Policy was used. The spectral dependences were measured in the wavelength range 400-1200 nm on an installation based on an MDR-3 grid monochromator and operating in the mode of a constant energy illumination level at the specimen's surface. Following the method expounded in work [12], the spectral characteristics that had been obtained were used to determine the effective diffusion length of minority charge carriers in the base region of SCs (it is a parameter which is crucial for the magnitude of the short circuit current  $I_{sc}$  and the SC efficiency).



Fig. 1. Dependences of the short circuit current on the  $\gamma$ -irradiation dose, normalized by their initial (before irradiation) values, for various SCs: mono-Si-based ones without a DLCF (1) and with it (2), and multi-Si-based ones without a DLCF (3) and with it (4). The inset represents the corresponding values for specimens 1 and 2 for a dose of  $10^5$  rad

In their turn, the LCVLCs were used to determine the following main photo-electric parameters of the SCs: the density of the short circuit current  $I_{\rm sc}$ , the opencircuit voltage  $V_{\rm oc}$ , the fill factor (FF) of the currentvoltage characteristic, and the SC efficiency  $\eta$ .

### 3. Experimental Results and Their Discussion

The analysis of the data obtained in our researches (see Figs. 1—6) gives rise to the following results.

1) At the  $\gamma$ -irradiation dose  $D = 10^5$  rad, the effect of radiation-induced ordering — an increase of the short circuit current through the SC at an invariable opencircuit voltage across it — was observed for SCs on the basis of mono-Si (Fig. 2). This phenomenon is explained by the increase of the diffusion length of minority charge carriers in the SC base region.

2) At small irradiation doses D, the following formula is valid [13]:

$$\frac{1}{L^2} - \frac{1}{L_0^2} = kD,\tag{1}$$

where  $L_0$  and L are the diffusion lengths of minority charge carriers in the initial specimen and after its  $\gamma$ irradiation, respectively; and k is the proportionality

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Fig. 2. Dose dependences of the open-circuit voltage across the SC, normalized by their initial values, for various SCs. The notations are the same as in Fig. 1. At a dose of  $10^5$  rad, curves 1 and 2 practically coincide

factor. The values of the latter for various specimens are given in Table 1.

3) For irradiation doses up to about  $10^7$  rad, the appreciable influence of  $\gamma$ -radiation on the values of the series and shunt resistances of the SC was absent, i.e. the fill factor of the CVC practically did not change. At exposure doses higher than  $10^7$  rad, a drastic deterioration of the FF for multi-Si-based SCs was observed. This follows from our results depicted in Fig. 3. 4) In the range of doses  $D \leq 10^6$  rad, the short circuit current  $I_{\rm sc}$  degraded more quickly in specimens fabricated on the basis of mono-Si. At  $D > 10^7$  rad, on the contrary, the degradation of short circuit current is stronger in specimens made up of multi-crystallite silicon (Fig. 1).

5) Within the whole studied range of  $\gamma$ -irradiation doses, the open-circuit voltage across the multi-Si-based SCs degraded more slowly than it was in the case of mono-Si

Fig. 3. Dose dependences of the fill factor of the SC current-voltage characteristic, normalized by their initial values, for various SCs. The notations are the same as in Fig. 1

ones (Fig. 2). As a result, at doses  $D \leq 10^6$  rad, the efficiency of the former degraded less than that of the latter.

6) Thermal annealing at T = 250 °C led to the deterioration of the parameters of SCs on the basis of mono-Si, which was caused by the formation of recombination-active complexes.

7) Thermal annealing at T = 400 °C led to the complete disappearance of defects generated by  $\gamma$ -radiation with an exposure dose of about  $10^7$  rad: for mono-Si-based SCs, the magnitudes of the quantities  $I_{\rm sc}$  and  $V_{\rm oc}$ returned back to their initial values or became even larger that the initial ones (Table 2).

8) The efficiency of the SCs with DLCFs degraded more slowly as compared with that of the SCs without DLCFs. This phenomenon was observed for SCs made up of silicon of either types (single- or multi-crystallite) (Fig. 4).

T a bl e 1. The values of the proportionality factor k for some specimens under investigation

Working notation (material) of a specimen	k	$\mathbb{N}^{\underline{o}}$ of the curve (specimen) in a figure
1k(mono-Si, without DLCF)	$1.508 \times 10^{-10}$	Figs. 1–4, curves 1, Fig. 5, curve 1
2k(mono-Si, without DLCF)	$1.442 \times 10^{-10}$	Fig. 5, curve $2$
70(mono-Si,  with DLCF)	$1.208 \times 10^{-12}$	Figs. 1–4, curves 2, Fig. 5, curve 3
156(mono-Si,  with DLCF)	$8.240 \times 10^{-12}$	Fig. 5, curve $4$
3(multi-Si, without DLCF)	$3.163 \times 10^{-10}$	Figs. 1–4, curves 3, Fig. 5, curve 5
F8-1(multi-Si, with DLCF)	$4.863 \times 10^{-11}$	
F6-1(multi-Si, with DLCF)	_	Fig. 1–4, curves 4, Fig. 5, curve $6$



Fig. 4. Dose dependences of the SC efficiency, normalized by their initial values, for various SCs. The notations are the same as in Fig. 1

On the basis of the data obtained, we can propose the following scenario of the defect formation in the SCs concerned which are subjected to irradiation with  $\gamma$ -quanta and the subsequent thermal annealing. While irradiating SC specimens with  $\gamma$ -quanta up to a dose  $D = 10^5$  rad, the radiation-induced ordering [14] takes place (the effect of small doses), and  $I_{\rm sc}$  increases for SCs based on mono-Si.

As the dose of irradiation grows further, the processes of formation of new radiation-induced defects associations "interstitial carbon ( $C_i$ , acceptor impurity) + oxygen  $(O_i)$ " - commence [15, 16]. These associations form recombination-active K-centers with the energy  $E = E_v + 0.35$  eV [1]. Owing to the growth of the K-center concentration, the diffusion length of minority charge carriers in the base region of SCs decreases (Fig. 5), which results in the degradation of  $I_{\rm sc}$  and  $V_{\rm oc}$  (Figs. 1 and 2). Recombination K-centers are formed uniformly over the volume of the crystal, which is evidenced by the faster degradation of  $I_{\rm sc}$  in comparison with that of  $V_{\rm oc}$  (Figs. 1 and 2) [17, 18], because the photocurrent  $I_{\rm sc}$  is determined mainly by the recombination parameters of the SC bulk, while the voltage  $V_{\rm oc}$  by the parameters of the near-surface region in the SC. This conclusion is confirmed by the results of measurements of the spectral dependences of the photocurrent; the relevant dependences typical of the mono-Si specimens are presented in Fig. 6. It is





Fig. 5. Dose dependences of the difference  $L^{-2} - L_0^{-2}$  (see Eq. (1)) for various SC specimens: mono-Si-based ones without a DLCF (1 and 2) and with it (3 and 4), and multi-Si-based ones without a DLCF (5) and with it (6). The parameters of the specimens are listed in Table 1



Fig. 6. Successive spectral characteristics of a single-crystalline solar cell with a diamond-like coating: (1) before  $\gamma$ -irradiation, (2) after  $\gamma$ -irradiation to a dose of 10<sup>7</sup> rad, and (3) after its annealing in argon at a temperature of 250 °C

evident from the figure that, after the specimen having been irradiated with  $\gamma$ -quanta to a dose of  $1.01 \times 10^7$  rad, the photocurrent and the steepness (the slope) of its spectral characteristic in the long-wave section of the spectrum (curve 2) decreased in comparison with their

SC material	Treatment	$J_{ m sc},{ m mA/cm^2}$	$V_{\rm oc}, V$	FF	$\eta, \%$
mono-Si without DLCF (1k)	initial	26	0.57	0.626	6.83
	$\gamma$ -irradiation, $D = 10^6$ rad	24.7	0.559	0.617	6.24
	$\gamma$ -irradiation, $D = 10^7$ rad	23	0.529	0.633	5.67
	$\gamma$ -irradiation+ annealing at 250°C	7.48	0.526	0.655	1.9
	$\gamma$ -irradiation+ annealing at 400°C	26.6	0.572	0.673	7.52
mono-Si with DLCF $(70)$	initial	34.2	0.573	0.748	10.8
	$\gamma$ -irradiation, $D = 10^6$ rad	33.6	0.566	0.757	10.7
	$\gamma$ -irradiation, $D = 10^7$ rad	31.2	0.541	0.759	9.39
	$\gamma$ -irradiation+ annealing at 250°C	13.2	0.541	0.758	3.99
	$\gamma$ -irradiation+ annealing at 400°C	33.3	0.57	0.754	10.6
multi-Si without DLCF $(3)$	initial	28.8	0.591	0.733	9.16
	$\gamma$ -irradiation, $D = 10^6$ rad	27.6	0.587	0.725	8.66
	$\gamma$ -irradiation, $D = 10^7$ rad	23.5	0.565	0.732	7.18
	annealing at 250 or 400 $^{\circ}\mathrm{C}$	back contact detachment			
multi-Si with DLCF (F6-1)	initial	33.2	0.586	0.681	9.81
	$\gamma$ -irradiation, $D = 10^6$ rad	32.2	0.581	0.685	9.43
	$\gamma$ -irradiation, $D = 10^7$ rad	28.9	0.567	0.682	8.26
annealing at 250 afo $400~^{\circ}\mathrm{C}$ back contact detach				chment	

T a b l e 2. Modification of SC paramete	r by $\gamma$ -irradiation and thermal ar	nnealing
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initial values (curve 1), which testifies for the reduction of the diffusion length of minority charge carriers (the deterioration of the recombination parameters) in the quasi-neutral volume (the base region) of the SC. At the same time, the short-wave sensitivity of the specimen practically was not changed (Fig. 6).

The weaker degradation of the efficiency of multi-Si-based SCs at doses  $D \leq 10^6$  rad is associated with the gettering of the defects that are formed, under irradiation with  $\gamma$ -quanta, at the grain boundaries, which serve as drains for radiation-induced defects (Table 2). A drastic reduction of the FF for such SCs at doses above  $10^7$  rad may be related to the partial detachment of the current-collecting contacts deposited by the screen printing method. A similar effect stimulates the sharp worsening of the FF for SCs based on multi-Si after their thermal annealing.

The heat treatment at T = 250 °C assisted the migration of interstitial  $C_i$  atoms over the Si crystal and a increase of the K-center concentration [1]. As a result, the further deterioration of  $I_{\rm sc}$  and  $V_{\rm oc}$  occurred for SCs made up of mono-Si. The photocurrent amplitude became smaller at that, and the slope of the spectral characteristics in the longwave range of the spectrum ( $\lambda > 800$  nm) got less steep (Fig. 6, curve 3), which reflects the reduction of the diffusion length of minority charge carriers in the quasi-neutral volume of the SC owing to the growth of the concentration of recombination Kcenters.

The heat treatment of the multi-Si-based SCs at T = 400 °C led to the practically complete annealing of K-centers and to the recovery of the photoenergetic

parameters and the diffusion length to their initial values or even to the values that exceeded the initial ones (Table 2).

The higher radiation resistance of SCs covered with a DLCF, which was observed for the specimens of both types within the whole investigated range of irradiation dose, is related, in our opinion, to the following reasons. The a-C:H and a-C:H:N films are known to contain a plenty of hydrogen atoms (up to tens of at.%) which form bonds mainly with carbons. Being subjected to high-energy  $\gamma$ -radiation, these bonds become partially broken. The released hydrogen atoms, while diffusing deep into the SC, passivate the broken bonds, which are recombination-active centers. As a result, the process of the SC parameter degradation becomes slowed down.

## 4. Conclusions

Thus, we have found that the radiation stability of SCs fabricated on the basis of silicon (single- and multicrystallite one) can be enhanced through depositing DLCFs enriched with hydrogen. It has been shown that the radiation stability of SCs made up of multicrystallite Si and subjected to  $\gamma$ -radiation to the exposure doses below 10<sup>6</sup> rad is higher than that of SCs fabricated on the basis of single-crystalline Si; this phenomenon takes place owing to the gettering of recombination-active defects and impurities by grain boundaries.

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#### ВПЛИВ 7-ОПРОМІНЕННЯ НА ПАРАМЕТРИ КРЕМНІЄВИХ СОНЯЧНИХ ЕЛЕМЕНТІВ

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Резюме

Досліджено механізми впливу радіаційного опромінення  $\gamma$ квантами дозами до  $10^8$  рад на рекомбінаційні і фотоенергетичні параметри сонячних елементів (СЕ), виготовлених на основі моно- та мультикристалітного кремнію, покритого та непокритого алмазоподібною вуглецевою плівкою (АВП). Показано, що к.к.д. сонячних елементів, покритих тонкою просвітлюючою АВП під дією  $\gamma$ -опромінення деградує менше порівняно з СЕ без АВП. Виявлено ефект гетерування рекомбінаційноактивних домішок межами зерен в СЕ на основі мультикристалітного Si при  $\gamma$ -опроміненні дозами  $D \leq 10^6$  рад.