SOLAR CELLS BASED UPON MULTICRYSTALLINE Si WITH DLC ANTIREFLECTION AND PASSIVATING COATINGS[2]

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The characteristics of multicrystalline Si solar cells covered by diamond-like carbon (DLC) antireflection coatings have been experimentally studied. It has been shown that this kind of coating provides a significant increase of the efficiency of solar cells mainly due to the increase of the short-circuit current density. The effects of antireflection and of the surface and bulk passivation on the SC current-voltage characteristics due to the DLC deposition have been investigated theoretically. Physical mechanisms underlying the observed effects have been proposed.

1. Introduction

One of the main tasks in the fabrication of multicrystalline silicon solar cells (SC) is the improvement of their parameters, particularly by the deposition of different antireflection and passivating coatings. A promising material for this purpose is diamond-like carbon (DLC). The optical properties of DLC films can be widely varied by the deposition technology allowing an optimum adjustment to the parameters of the substrate. A significant influence of nitrogen added to the gas mixture during the DLC film deposition on film properties was noted in some previous publications [1—3]. The optical and mechanical characteristics of DLC films derived by the plasma-enhanced chemical vapour deposition (PE—CVD) were investigated in dependence on the nitrogen concentration in the gas mixture in [2,3]. The antireflection effect of DLC films on the Si solar cell performance has been studied theoretically in [4].

In the present work, the characteristics of multicrystalline Si solar cells covered by DLC films have been investigated experimentally. A theoretical analysis of the antireflection, as well as of the bulk and surface passivation mechanisms produced by DLC films, has been carried out to reveal the physical mechanisms of the influence of DLC layers on the multicrystalline Si solar cell performance.

2. Experimental Procedure

The solar cells studied were made of multicrystalline p-type Si wafers with a resistivity of 1 Ω·cm. The SCs were produced by using two technological routes. The technological process included $POCl_3$ diffusion (routes 1, 2), thermal oxidation (SiO_2 of 20 nm in thickness) (route 1), Al gettering on the rear side (Al layer was etched away after the gettering) (route 1), photolithographic deposition of Ti/Pd/Ag (route 1) or screen printing Ag based contacts on the front (route 2), evaporation of 2 μm Al (route 1) or screen printing Al contacts (route 2) on the back.

DLC films were deposited by PE-CVD using a setup with a capacitance reactor. A gas mixture consisting of CH_4, N_2, and H_2 was used. The deposition was carried out at 125-W discharge power, with a deposition time of 3 min selected to provide the optimum thickness of the antireflection coating. The film thickness was measured by a laser ellipsometer "LEF-3M" and a profilometer "Dektak" (∼5-nm accuracy of the thickness determination).

The spectral dependences of the short-circuit current were measured by a certified spectral setup in the regime of constant photon flux. The measurements were performed in the spectral range from 0.2 to 1.2 μm. Measurements of light current-voltage (I—V) characteristics of solar cells were also performed.

3. Calculations

Calculations have been performed to study the physical mechanisms responsible for the substantial increase of

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the solar cell efficiency caused by the DLC films. Three effects have been considered, namely: (i) increase of the light flow on a solar cell due to the antireflection effect of the DLC film, (ii) change of the surface recombination velocity, and (iii) change of the diffusion length of minority carriers (holes in the emitter region and electrons in the base region, respectively). The direction of a change of two latter parameters cannot be determined at first glance since the recombination properties both at the surface and in the bulk of silicon can be improved due to the passivation of recombination-active centers by hydrogen during the plasma treatment or the DLC film deposition, or deteriorate as a result of the plasma-induced damage.

To study the antireflection effect provided by the DLC film, the ampere-watt sensitivity of a DLC-coated solar cell has been calculated and compared to the experimental results obtained for a solar cell prior to and after the DLC film deposition. The transmission coefficients of the 20-nm SiO_2 coating of the solar cell prior to the DLC film deposition and of the 70-nm DLC film have been calculated by recurrent formulas of the optical model for the system consisting of a Si active layer, film coating, and surrounding air [5]. The ampere-watt sensitivity of a solar cell after the DLC film deposition, $P_{\rm DLC}(\lambda)$, has been calculated using the measured sensitivity of the solar cell prior to the deposition of the antireflection coating, $P_{\rm SiO2}(\lambda)$:

$$P_{\rm DLC}(\lambda) = P_{\rm SiO_2}(\lambda)\frac{T_{\rm DLC}(\lambda)}{T_{\rm SiO_2}(\lambda)}, \qquad (1)$$

where $T_{\rm SiO_2}(\lambda)$ and $T_{\rm DLC}(\lambda)$ are the transmission coefficients of the solar cell coatings prior to and after the DLC film deposition, respectively.

The measured ampere-watt sensitivity $P_{\rm measur}$ is reduced relative to the maximum one due to that not all the light incident on the solar cell contributes to the charge birth, but its part is reflected and absorbed in the antireflection film. The ampere-watt sensitivity in the case where the entire incident light contributes to the current formation is related to the measured one as follows: $P = P_{\rm measur}\ /\ T$ with T being the transmission coefficient of the antireflection coating. Applying this relation to the case of DLC and SiO_2, we obtain $P_{\rm SiO_2}\ /\ T_{\rm SiO_2} = P_{\rm DLC}\ /\ T_{\rm DLC}$, from which formula (1) follows.

In our analysis of current-voltage characteristics, we neglected the recombination current in the space charge region, since its thickness is considerably smaller than the diffusion lengths of charge carriers (the so-called "thin" $p-n$-junction [6]). Indeed, the maximum width of a barrier layer, w, at the zero applied voltage can be calculated by the formula [7]

$$w = \sqrt{\frac{2\varepsilon_0\varepsilon U_d(N_d+N_a)}{eN_dN_a}}, \qquad (2)$$

where ε_0 and e are the dielectric constant and electron charge, respectively, ε is the Si permittivity, U_d is the diffusion voltage,

$$U_d = \frac{kT}{e}\ln\frac{N_dN_a}{n_i^2}, \qquad (3)$$

N_d and N_a are the doping levels of the emitter and the base of a solar cell, respectively, and $n_i = 1.4\times10^{10}$ cm^{-3} is the intrinsic concentration of charge carriers in silicon [6].

For our case, $N_d \approx 10^{19}$ cm^{-3} and $N_a \approx 1.25\times10^{16}$ cm^{-3}. The maximum width of the barrier region is, accordingly, about 0.3 μm, while the typical values of the diffusion length of charge carriers in multicrystalline silicon are $\sim$ 50—100 μm [8]. The approximation of a thin $p-n$-junction is therefore justified.

The current produced by a solar cell is the difference between the current generated by the flow of light quanta onto the solar cell and the recombination current [7]. Therefore, the following expression can be written for the current density of the solar cell:

$$J(U) = J_g(U) - J_r(U) = \int\limits_{\lambda_{\min}}^{\lambda_{\max}} j_g(U,\lambda)n(\lambda)d\lambda - J_r(U), \qquad (4)$$

where $J_g(U)$ and $J_r(U)$ are the generation and recombination current densities, respectively, U is the forward voltage applied to the solar cell, $n(\lambda)$ is the number of photons per unit wavelength penetrating into the active layer of the solar cell per unit area and unit time, while $\lambda_{\min} \approx 0.4$ μm and $\lambda_{\max} \approx 1.2$ μm determine the range where Si has a non-zero sensitivity. We do not write the full expressions for $J_r(U)$ and $J_g(U)$ since they are too cumbersome.

Assuming that the Sun's radiation is that of the absolutely black body with a temperature of 5760 K [7], the quantity $n(\lambda)$ can be calculated by dividing the Planck's function for the spectral radiation density by the photon energy:

$$n(\lambda) = \frac{2\pi hc^2}{\lambda^5}\frac{\xi}{\exp\left(\frac{hc}{\lambda k\cdot 5760}\right)-1}\frac{\lambda}{hc} =$$

$$= \frac{2\pi c}{\lambda^4}\frac{\xi}{\exp\left(\frac{hc}{\lambda k\cdot 5760}\right)-1}. \qquad (5)$$

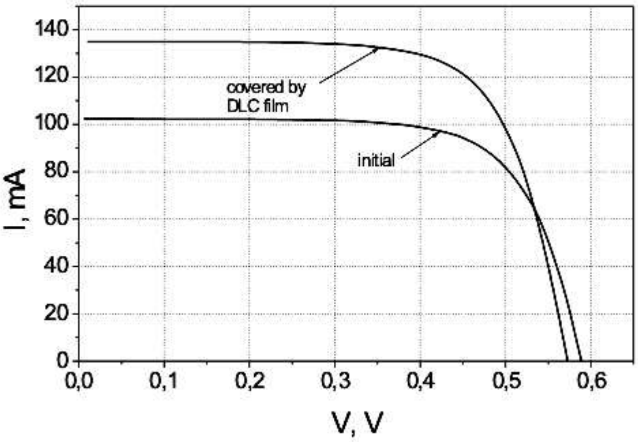

Fig. 1. Experimental current–voltage characteristics of a multicrystalline Si solar cell in the initial state and with a DLC antireflection coating deposited at 20 % nitrogen in the gas mixture, respectively. The characteristics correspond to samples 1 and 1a in Table 1

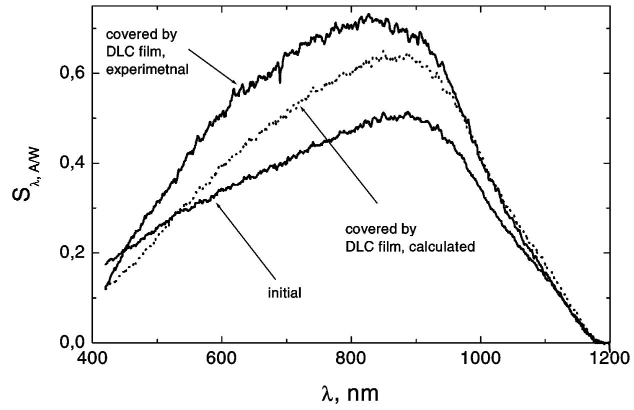

Fig. 2. Ampere–watt sensitivities of a multicrystalline Si solar cell: measured sensitivity in the initial state (20-nm SiO_2), measured sensitivity after the deposition of a 70-nm thick DLC antireflection coating (20 % nitrogen in the gas mixture), sensitivity calculated using the optical parameters of the DLC film. The experimental curves correspond to samples 1 and 1a in Table 1

Here, h is Planck's constant, c is the light velocity in vacuum, k is Boltzmann's constant, and $\xi \approx 2.2\times10^{-5}$ is a dimensionless parameter which is determined by normalizing the Sun's radiation power per 1 m^2 at the surface of the Earth to 1360 W [9].

4. Results and Discussion

The solar cells studied in this work have been covered with DLC films obtained with 20 % nitrogen content in the gas medium. The typical current—voltage characteristics of solar cells prior to and after the DLC film deposition (70 nm) are presented in Fig. 1. The respective ampere—watt sensitivities are presented in Fig. 2. In Table 1, the parameters of the solar cells based on multicrystalline Si not covered and covered by DLC antireflection coatings are given. A significant increase of the short-circuit current after the deposition of an antireflection DLC film is observed for the SCs obtained by using technological route 1 (Fig. 1,*a*, Table 1, sample 1a) and route 2 (Table 1, sample 2a) demonstrating a decrease of light reflection losses and the good DLC film antireflection effect. For both routes, the SCs fill factor is not changed. Moreover, the DLC film demonstrates a good passivating influence on the SC surface. Such an efficient passivation of surface recombination centers is provided by the hydrogen plasma treatment prior to the deposition process and a high concentration of hydrogen in the DLC film that terminates dangling bonds and defects in the silicon wafer. It should be noted that the efficiency of SC increases up to 1.3 times after the deposition of DLC films. The deposition of a DLC film leads to the increase of the spectral sensitivity practically in the whole range of $\lambda = 475 \div 1100$ nm (Fig. 2). For the SC produced by using route 2 (SC with bare surface), the open-circuit voltage increases demonstrating the DLC film passivating effect. Some decrease of the open-circuit voltage for the SC produced by using route 1 (SC with a thin SiO_2 passivating layer) is probably connected with the radiation-induced damage of the SiO_2 layer during the plasma treatment prior to the DLC film deposition. Another explanation of this effect, namely the increase of the contact series resistance as a result of the DLC deposition seems less probable for the technology used.

T a b l e 1. Experimental parameters of multicrystalline Si solar cells without (1, 2) and with (1*a*, 2*a*) DLC antireflection coatings

Sample	Spectral conditions	I_{sc}, mA	J_{sc}, mA/cm^2	V_{oc}, V	FF	η, %
1[1]	AM1.5	102	25.6	0.589	0.709	10.4
1a[1]	AM1.5	135	33.7	0.573	0.709	13.3
2[2]	AM1.5	270	27.0	0.571	0.733	11.2
2a[2]	AM1.5	323	32.3	0.581	0.733	13.5

* [1] and [2] correspond to the respective technological routes of cell fabrication.

The calculated ampere-watt sensitivity of a solar cell covered by a diamond-like antireflection coating is also presented in Fig. 2 together with experimental data measured prior to and after the DLC film deposition. It can be seen that the calculated curve runs lower than the experimental curve measured after the DLC

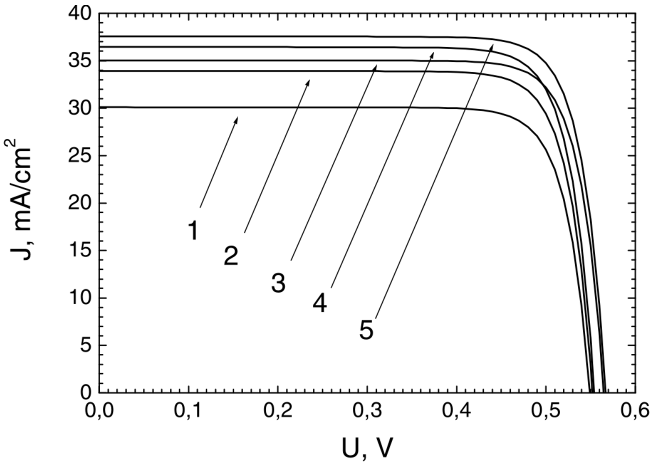

Fig. 3. Calculated current-voltage characteristics of multicrystalline Si solar cells not covered (*1*) and covered with DLC films (*2—5*). The parameters of calculations are shown in Table 2

deposition if we take into account only a change of the light penetration into the Si active layer due to the antireflection effect. This means that other mechanisms, in addition to antireflection, take part in raising the efficiency of the light conversion in DLC-covered Si solar cells.

It is known that the recombination properties of multicrystalline silicon are worse than those of monocrystalline Si due to the presence of a great number of recombination-active centers in grains and at the grain boundaries. The diffusion lengths of minority carriers in multicrystalline Si are comparatively lower than those in single-crystalline Si ($\sim$ 100 μm vs. $\sim$ 1000 μm). In our previous papers [10, 11], we demonstrated that the grain boundary recombination is insignificant for the solar cell performance in the case of multicrystalline silicon (grain sizes in the millimeter range), so the principal attention should be given to the recombination in grains. The passivation of these recombination-active centers in the bulk, as well as on the surface, leads to an increase of the photocurrent produced by the solar cell.

T a b l e 2. The parameters used in the calculation of the current-voltage characteristics of multicrystalline Si solar cells covered by DLC films

Parameter	Number of calculation*				
	1	2	3	4	5
Diffusion length of holes in the emitter region, μm	0.5	0.5	1.0	0.5	1.0
Diffusion length of electrons in the base region, μm	50	50	100	50	100
Surface recombination rate, cm/s	10^5	10^5	10^5	10^4	10^4
Open-circuit voltage, V	0.549	0.552	0.565	0.554	0.567
Short-circuit current density, mA/cm^2	30.11	33.93	35.04	36.45	37.56

*The numbers refer to the curves shown in Fig. 3.

DLC films contain a great concentration of hydrogen, which is defined by the technology of their deposition [1—3]. Hydrogen can passivate the bulk and surface recombination-active centers and thus leads to an improvement of the solar cell output characteristics. The treatment of the samples in hydrogen plasma prior to the DLC film deposition results in the additional passivation of recombination-active centers. However, the plasma can also induce a damage, which can lead to the degradation of the solar cell characteristics.

We have investigated the effect of surface passivation (a decrease of the surface recombination rate) and bulk passivation (an increase of the minority diffusion length) on the current-voltage characteristics of multicrystalline Si solar cells theoretically. The results are presented in Fig. 3. There is no precise correlation between the experimental and calculated current-voltage characteristics since we did not tie ourselves to the parameters of real solar cells. The values of the parameters used in the calculations presented in Fig. 3 are shown in Table 2. As can be seen from Fig. 3, the decrease of the surface recombination rate has a principal impact on the short-circuit current density, while the increase of the diffusion length of minority carriers influences both the current and the open-circuit voltage. The passivation of both surface and bulk recombination-active centers can lead to an increase of the short-circuit current density by about 1.3 times, what is indeed observed experimentally.

5. Conclusion

In the present work, it has been demonstrated that the DLC film coating provides a significant increase of the short-circuit current density of multicrystalline Si solar cells. Reducing the light radiation losses caused by the reflection from the front surface of a solar cell is one of the key factors of the positive effect observed. The passivation of surface and bulk recombination centers by hydrogen during the pre-deposition plasma treatment and after the DLC film deposition can result in additional improvements, which has been shown from the theoretical analysis of the mechanisms influencing the current-voltage characteristics.

Note that the color spottiness of the surface of multicrystalline silicon is probably related to a different microstructure (texturing) of the surface of grains. The influence of this effect on the characteristics of multicrystalline Si solar cells can be analyzed by using the Gaussian distribution for the light absorption throughout the cell surface. In this work, we have neglected the surface differences in reflectivity and used the homogeneous light absorption model.

In conclusion, the results of the experimental and theoretical studies of DLC-covered multicrystalline Si solar cells show that the DLC films are very promising antireflection and passivating coatings for such a kind of solar cells.

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СОНЯЧНІ ЕЛЕМЕНТИ НА ОСНОВІ МУЛЬТИКРИСТАЛІТНОГО КРЕМНІЮ З АПВ АНТИВІДБИВНИМИ ТА ПАСИВУЮЧИМИ ПОКРИТТЯМИ

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Р е з ю м е

Експериментально досліджено характеристики сонячних елементів (СЕ) на основі мультикристалітного кремнію, покритих алмазоподібними вуглецевими (АПВ) просвітлюючими плівками. Показано, що такі покриття забезпечують суттєве збільшення к.к.д. сонячних елементів головним чином завдяки збільшенню густини струму короткого замикання. Теоретично проаналізовано вплив просвітлення та пасивації поверхні і об'єму на вольт-амперні характеристики СЕ при осадженні АПВ-плівок. Проаналізовано фізичні механізми ефектів, що спостерігались.