J. Phys. D: Appl. Phys. **37** (2004) L25–L28 PII: S0022-3727(04)81308-1

RAPID COMMUNICATION

Low reflectance of diamond-like carbon/porous silicon double layer antireflection coating for silicon solar cells

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Received 26 May 2004, in final form 17 August 2004
Published 15 September 2004
Online at stacks.iop.org/JPhysD/37/L25
doi:10.1088/0022-3727/37/19/L01

Abstract
Reflectance calculations for diamond-like carbon (DLC) antireflection thin-film coatings on porous silicon (PS) have been carried out using the optical matrix approach method. Comparison with the reflectance spectrum obtained for other antireflection coatings shows a much lower reflectance with a larger energy range including the ultraviolet, visible and infrared regions of the solar spectrum for the DLC/PS double layer. This finding is relevant in solar cell applications.

One of the crucial problems in solar cells is that a significant part of the incoming radiation is reflected, which limits the efficiency of such devices. One of the important ways of minimizing this detrimental effect and subsequently improving the characteristics is reduction of the reflectance with an appropriate thin film coating. Such an approach serves to increase the absorbed part of the solar irradiation in the whole optical and near-IR region when the corresponding antireflection coating has an appropriate refractive index (n) and layer thickness (d).

The use of silicon in solar cell technology is well established. Unfortunately, the efficiencies achieved are lower than initially expected. Indeed, antireflection coatings are appropriate for increasing not only light absorption but also radiation in a wider energy range, thus covering a broader range of the solar spectrum. This leads to a significant efficiency improvement by about ≈40–44%, especially important for Si-based solar cells because Si reflects approximately 30% of the incident light in the spectral range where Si is photosensitive. For this purpose, the most widely used technique in industrial applications is a combination of chemical texturization [1, 2] using an alkaline etch (for instance NaOH aqueous solution) and deposition of antireflection coatings, homogeneous thin film layers of a transparent medium having a refractive index n between those of air ($n = 1$) and Si ($n = 3.5$). However, due to random grain orientations, the alkaline etch remains rather ineffective. Different types of single- or multilayer ARCs are used to more or less address the problem of low reflectance [3, 4]. It could in particular include ZnS, Al_2O_3, Ta_2O_5 layers using a single-layer ARC, double-layer ARCs, SiO_2/TiO_2 and MgF_2/ZnS, and triple-layer ARC MgF_2/Al_2O_3/ZnS coatings. However, these materials are not suitable because magnesium fluoride and zinc sulfide are relatively soft and easily damaged and eroded by rain, wind and particle impact. They also have poor resistance to corrosive environments [5, 6], leading to degradation of the solar cell parameters with time. In addition, some oxide layers have inappropriate refractive indexes and/or low transparency (especially for Ta_2O_5, compared with ZnS), making them unsuitable for ARC materials. Besides, a texturization step is necessary before deposition of such layers. Therefore, the surfaces of crystalline silicon solar cells are usually textured to reduce the surface reflectance [1–3]. Several approaches have been proposed for efficiently reducing the reflectivity, like laser scribing and mechanical texturization, but so far, the corresponding technical and cost requirements are not consistent with the large volume production necessary in applications.

Coatings made of porous silicon (PS) layers are of special interest [7]. Indeed, PS (i) leads to a reduction in reflectance [8], (ii) a reduction in surface recombination velocity, (iii) enlarges the spectral sensitivity region and (iv) improves photo-generation of carriers. PS can be easily formed on the emitter part of a solar cell by electrochemical anodization in HF-containing solutions without using any complicated technological methods. As such layers are grown on the same material (silicon), it is possible to manufacture a selective emitter and ARC in one step simultaneously, replacing a three-step processing: texturization, passivation and ARC deposition. Besides, the use of PS leads to a 20–50% increase in the solar cell short-circuit current [9]. Because of its porous nature, the PS refractive index depends on the porosity and can vary from 1.25 to 3, allowing many applications of this material, e.g. as Fabry–Pérot filters, Bragg mirrors, planar waveguides or microcavities [10]. A substantial reflectivity reduction was achieved on a multicrystalline silicon solar cell substrate after a dynamic PS etching procedure [11].

However, PS has a drawback, the degradation of its parameters with time, if special methods to preserve the PS properties are not used. It is necessary to protect PS from ambient air by covering with other layers to prevent degradation. In this context, diamond-like carbon (DLC) films are of great interest, since they have very high hardness, a high stability in hostile environments such as in aggressive chemical attacks, under irradiation or under ambient condition fluctuations: there is very little change ($\sim$0.03%) in the efficiency of silicon solar cells with DLC films after exposure to a relative humidity of 90% at 90°C for 20 h. It is known also that the hardness of DLC films does not change when the temperature rises up to 300°C [12]. The technology of DLC film growth is well established using CVD from hydrocarbon precursors and sputtering of a graphite target [13] on the PS layer [14, 15]. Note also that the deposition of DLC layers occurs at low temperatures (in some technologies, it does not exceed $\sim$300°C), therefore leading to no changes in the properties of silicon solar cells. It is possible, of course, to obtain porous and non-porous DLC coatings. Non-porous DLC coatings mainly act as a protective coating for PS and allow us to reduce the reflectance in the short-wavelength region. In addition to the properties mentioned above, porous DLC can effectively trap light on silicon, which can actually give rise to an increase in the solar cell efficiency. Such a combination of properties allows us to use this advanced material as a protective thin film coating. In addition, by changing the growth parameters, it is possible to change the refractive index of such a material from 1.6 to 2.7 [16]. Furthermore, due to a large band gap, DLC has a high transparency in the UV region, making it especially promising in solar cells for space applications [17].

In this Rapid Communication, we use DLCs to explore ARCs having advanced properties in silicon solar cells. Using the optical matrix approach method, we calculate the reflectance of DLC thin films on PS. Compared with the reflectance obtained for other ARCs, we find a much lower reflectance in the UV, visible and IR regions of the solar spectrum for a DLC/PS double layer, indicating the strong interest of the latter for solar cell applications.

We use the optical matrix approach for the calculation [18, 19]. A plane wave interacting with a stack of thin layers is considered. So

$$E = E_0\,\mathrm{e}^{\mathrm{i}kr-\mathrm{i}\omega t}, \qquad H = H_0\,\mathrm{e}^{\mathrm{i}kr-\mathrm{i}\omega t}, \tag{1}$$

where E and H are the electrical field's and the magnetic field's strengths, respectively, E_0 and H_0 are their amplitude, k is a wave vector and ω is the frequency of the incident light.

We let the thin layers have different refractive indexes. Inside each layer, the Maxwell equations become

$$k \times E_0 = \left(-\frac{\omega}{c}\right) \times H_0, \quad k \times H_0 = \left(-\frac{\omega n^2}{c}\right) \times H_0. \tag{2}$$

The boundary conditions at the interface of two layers having different refractive indexes n_1 and n_2 are:

$$(E_0)_{\tau_1} = (E_0)_{\tau_1}, \qquad n_1(e_k \times E_0)_{\tau_1} = n_2(e_k \times E_0)_{\tau_2}, \tag{3}$$

where the subscript τ denotes the tangential component with respect to the boundary and e_k shows the direction of the wave propagation. For simplicity we consider normal incidence of light with plane polarization. Let the z-axis be directed normal to the stack of layers and the x-axis directed along the polarization of the light. Then the resulting wave field takes in any layer (denoted by j) the following form:

$$E_j = e_x[(E_+)_j\,\mathrm{e}^{\mathrm{i}k_j z} + (E_-)_j\,\mathrm{e}^{-\mathrm{i}k_j z}]. \tag{4}$$

The boundary conditions (equation (3)) can be rewritten in the matrix form,

$$\hat{S}_1 \begin{pmatrix} E_+ \\ E_- \end{pmatrix}_1 = \hat{S}_2 \begin{pmatrix} E_+ \\ E_- \end{pmatrix}_2, \tag{5}$$

where the surface matrices are equal,

$$\hat{S}_j = \begin{pmatrix} 1 & 1 \\ n_j & -n_j \end{pmatrix}. \tag{6}$$

The diagonal phase matrix $\hat{\Phi}_j$ connects the fields $E_j(z)$ at the opposite surfaces of the layer j,

$$\hat{\Phi}_j = \begin{pmatrix} \mathrm{e}^{\mathrm{i}k_j d_j} & 0 \\ 0 & \mathrm{e}^{-\mathrm{i}k_j d_j} \end{pmatrix}, \tag{7}$$

where d_j is the layer thickness and $k_j = n_j\omega/c$ is the wave number of j layers. Each layer is considered separately. Then, the field behind the layer can be straightforwardly expressed in terms of the field:

$$\begin{pmatrix} E_+ \\ E_- \end{pmatrix}_{\mathrm{final}} = (\hat{S}_\mathrm{a})^{-1}\hat{S}_j\hat{\Phi}_j(\hat{S}_j)^{-1}\hat{S}_\mathrm{a}\begin{pmatrix} E_+ \\ E_- \end{pmatrix}_{\mathrm{initial}}, \tag{8}$$

where the subscript 'a' is related to the environmental area.

Following the same path, we easily obtain the expression for all stacks of N layers:

$$\begin{pmatrix} E_+ \\ E_- \end{pmatrix}_{\mathrm{final}} = (\hat{S}_\mathrm{a})^{-1}\hat{B}_N\hat{B}_{N-1}\hat{B}_{N-2}\cdots\hat{B}_1\hat{S}_\mathrm{a}\begin{pmatrix} E_+ \\ E_- \end{pmatrix}_{\mathrm{initial}} \tag{9}$$

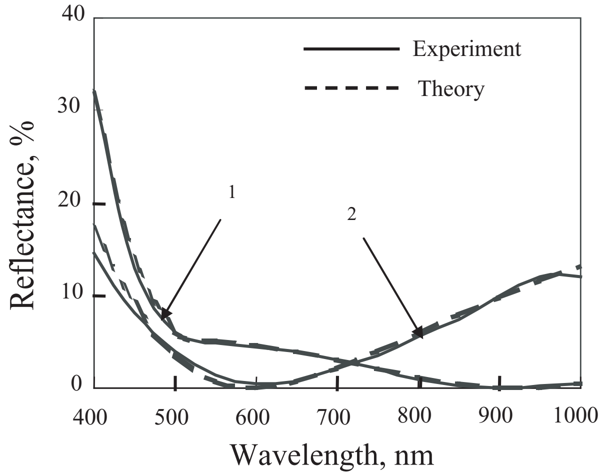

Figure 1. Experimental and calculated reflectance versus wavelength of the MgF_2/ZnS (1) and SiO_2/TiO_2 (2) double layer coatings.

with the layers' matrices

$$\hat{B}_j = \hat{S}_j \hat{\Phi}_j (\hat{S}_j)^{-1} = \begin{pmatrix} \cos\varphi_j & \mathrm{i}\dfrac{\sin\varphi_j}{n_j} \\ \mathrm{i}n_j \sin\varphi_j & \cos\varphi_j \end{pmatrix},$$

$$\varphi_j = n_j \frac{\omega}{c} d_j. \tag{10}$$

The transmission and reflection coefficients are determined by the following expression:

$$T = \left| \frac{(E_+)_f}{(E_+)_i} \right|^2 = |t|^2, \qquad R = \left| \frac{(E_-)_i}{(E_+)_i} \right|^2 = |r|^2. \tag{11}$$

This method allows us to calculate the properties of different types of ARC using 'Mathematica-4', a simple software.

As mentioned above, double layer ARCs (MgF_2/ZnS and SiO_2/TiO_2 coatings) are used in solar cells, which leads to a spectrum range increase and a rather low reflectance, therefore improving the overall performance of the solar cells. We also calculate the reflectance spectrum for such coatings using the optical matrix method mentioned above and compare the results of the calculations with experimental ones [3, 20, 21] (figure 1). As can be seen clearly, the theoretical calculations and experimental results are in very good agreement for these double layer coatings. However, these coatings can absorb a maximum of 47% of the solar irradiation. Therefore, it is necessary to design an ARC having a low reflectance in the UV region also. For this purpose, PS has an advantage, since it can be prepared easily by electrochemical anodization. By accurate and smooth changing of electrochemical parameters (current density, anodization time and others), it is possible to vary the layer porosity and, hence, optical properties, which allows many optical applications of this material. Moreover, the application of PS leads to a significant reduction in the reflection, increasing the spectral sensitivity region, improving the photo-generation of carriers, leading to an overall improvement of the solar cell performance. There is the Bruggeman effective medium approach, which allows us to examine PS with its complex three-dimensional surface as a homogeneous layer with a certain refractive index. Even

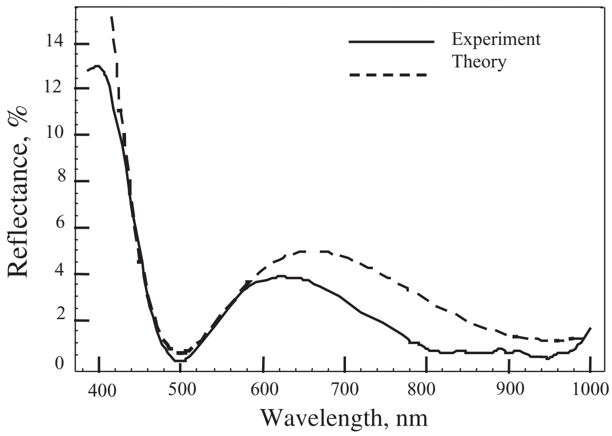

Figure 2. Simulation of the reflectance of a PS penta-layer.

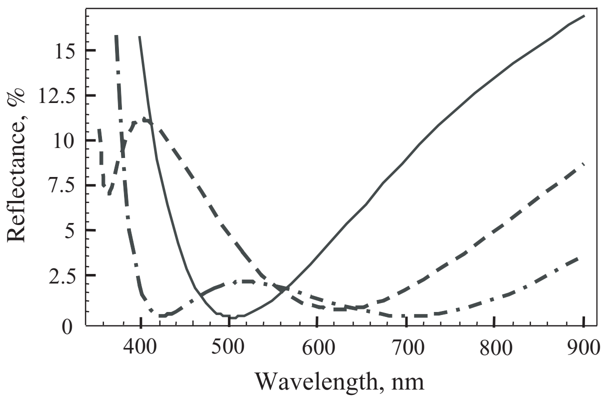

Figure 3. Reflectance spectra of single layer DLC (——) and DLC/PS double layer coatings: ($n_{DLC} = 1.6$; $n_{PS} = 2.9$; $d_{DLC} = 85$ nm; $d_{PS} = 30$ nm, $\cdots\cdots$) and ($n_{DLC} = 1.6$; $n_{PS} = 2.8$; $d_{DLC} = 86.9$ nm; $d_{PS} = 47.9$ nm, — · —).

if we obtain a PS layer that has a depth inhomogeneity, we can consider such a layer as a stack of several layers with certain refractive indexes. Figure 2 displays the theoretical and experimental reflectance spectrum of a PS thin film [22].

It is interesting to note that the use of the DLC film as a single layer ARC improves the characteristics of solar cells with, however, no reflectance reduction in the UV region (figure 3, solid line) [16].

In order to explore the possible reduction of the reflectance in the UV region, we calculated the reflectance of a multilayer coating made of DLC/PS double layers using again the same optical matrix approach. To find the desired value of the refractive indexes and the thickness of the layers, the calculation was carried out for several values, and then we selected two cases. In first case (figure 3, dotted line) the parameters of the layers were chosen as $n_{DLC} = 1.6$; $n_{PS} = 2.9$; $d_{DLC} = 85$ nm; $d_{PS} = 30$ nm. The result shows that the use of such a DLC/PS structure is non-effective because of higher reflectances in the IR and visible regions, while a rather low reflectance is achieved in the UV region.

In the second case (figure 3, dash–dotted line), the parameters of the layers were chosen as $n_{DLC} = 1.6$; $n_{PS} = 2.8$; $d_{DLC} = 86.9$ nm; $d_{PS} = 47.9$ nm. With such parameters, the calculation shows that the low reflectance in the IR region is not only preserved, but also enlarged towards the short-wave region (up to 400 nm). This implies that application of this coating in solar cells is especially effective. The enlargement of range with almost zero reflectance leads to a large increase in the absorbed part of the solar irradiation (this value can rise up to 60%), leading to a very significant increase in solar cell efficiency.

In conclusion, we have calculated the reflectance spectrum of DLC/PS and other ARCs using the optical matrix approach method. This simulation allows comparison of the DLC/PS double layer with other ARCs and shows that this coating is characterized by a much lower reflectance in the infrared, visible and ultraviolet spectral range. These features, combined with high stability parameters and the ability to work in hostile environments, make the DLC thin film coating especially promising for solar cell applications.

Acknowledgments

This work has been supported by the ISTC A-322 grant, by the Armenian National Program No 041030 and by the Ministère des Affaires Etrangères of France, through the COCOP programme with the Commissariat à l'Energie Atomique (CEA-Saclay).

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