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Application of amorphous carbon based materials as antireflective coatings on crystalline silicon solar cells

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We report on the investigation of the potential application of different forms of amorphous carbon (a-C and a-C:H) as an antireflective coating for crystalline silicon solar cells. Polymeric-like carbon (PLC) and hydrogenated diamond-like carbon films were deposited by plasma enhanced chemical vapor deposition. Tetrahedral amorphous carbon (ta-C) was deposited by the filtered cathodic vacuum arc technique. Those three different amorphous carbon structures were individually applied as single antireflective coatings on conventional (polished and texturized) p-n junction crystalline silicon solar cells. Due to their optical properties, good results were also obtained for double-layer antireflective coatings based on PLC or ta-C films combined with different materials. The results are compared with a conventional tin dioxide (SnO_2) single-layer antireflective coating and zinc sulfide/magnesium fluoride (ZnS/MgF_2) double-layer antireflective coatings. An increase of 23.7% in the short-circuit current density, J_{sc}, was obtained using PLC as an antireflective coating and 31.7% was achieved using a double-layer of PLC with a layer of magnesium fluoride (MgF_2). An additional increase of 10.8% was obtained in texturized silicon, representing a total increase (texturization + double-layer) of about 40% in the short-circuit current density. The potential use of these materials are critically addressed considering their refractive index, optical bandgap, absorption coefficient, hardness, chemical inertness, and mechanical stability. © *2011 American Institute of Physics*. [doi:10.1063/1.3622515]

I. INTRODUCTION

Photovoltaic energy is considered to be a great resource in combating the harmful effects caused by conventional sources of energy based upon non-renewable fossil fuels along with diversifying the energy matrix around the world. However, some stages in the fabrication of photovoltaic devices involve toxic materials, thereby requiring controlled disposal of the residues. An antireflective layer, for instance, may use a compound such as silane (SiH_4), or elements such as tin (Sn), indium (In), and other elements that need special care during solar cell manufacturing, or has limitations related to natural abundance or contamination of the environment. Due to these concerns, some researchers have investigated the use of antireflective coatings based on amorphous carbon,[1–9] an extremely abundant and environmentally sound element.

Amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H) are a class of materials which can be used in several applications due to their various physical and chemical properties, such as high mechanical hardness, high optical transparency in the visible and near infrared, high thermal conductivity, low friction coefficient, and chemical inertness to some corrosive agents.[10–13] They have been extensively proposed and used in a large variety of applications as protective tribological coating, radiation protection, electron field emitters, and in biomedicine.[14–20]

Reported works on the use of amorphous carbon as an antireflective coating do not give much detail concerning the structure of the film. As is well known, the properties of amorphous carbon strongly depend on the technique and on the deposition condition. Films deposited by sputtering usually have a high concentration of sp^2 hybridized carbon (sp^2 C) and a very low bandgap, resembling the properties of graphite. Due to these properties, this material is referred to as graphite-like carbon (GLC) and is not suitable as an antireflective coating. The properties of films deposited by plasma enhanced chemical vapor deposition (PECVD) depend very much on the applied bias voltage. For low negative bias voltage (<-40 V) the films are very soft, have a high bandgap (>2.5 eV), a low mechanical stress, and a high concentration of hydrogen (40–60 at. %) bonded to sp^3 hybridized carbon (sp^3 C). These films are usually referred to as polymeric-like carbon (PLC). For intermediate bias voltage (-50 to -300 V) the films are hard, have an intermediate bandgap (1–2 eV), relatively high stress (1–3 GPa), high hardness (10–30 GPa) and an intermediate content of sp^3 sites (20–60%). These films are usually referred to as diamond-like carbon (DLC). On the contrary, films deposited at a higher bias voltage have an even lower fraction of sp^3 sites and are almost gapless, being referred to as graphite-like carbon (GLC). Amorphous carbon with a high concentration of sp^3 sites (60–95%) have been deposited by filtered cathodic vacuum arc (FCVA) and laser ablation.[21–28] These films have a relatively high bandgap (1.5–2.5 eV), are extremely hard (40–90 GPa), and extremely stressed (5–15 GPa). These films are known as tetrahedral amorphous carbon (ta-C).

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In a previous work, Oliveira, Jr. *et al.*[6] reported on the use of those different forms of amorphous carbon films (PLC, DLC, and ta-C) as antireflective coatings on crystalline silicon solar cells. In the present work we extend the investigation to double-layer antireflective coatings on polished and on texturized silicon surfaces and critically address the main problems related to the use of these materials as potential candidates for antireflective coatings on crystalline silicon solar cells. In addition, we also investigate the use of a silicon-carbon alloy as an antireflective coating. We adopt the usual nomenclature for the amorphous carbon structures, i.e., DLC, PLC, and ta-C, to be consistent with literature and to better identify the differences in the structures of amorphous carbon. For the PLC films, this work is restricted to films deposited by PECVD with methane (CH_4), since this type of material comprises a large variety of structures. Graphite-like films will not be considered in this work since their optical bandgap is very low or zero. Emphasis will be placed on the optical bandgap and the refractive index, which are important parameters that have not been sufficiently considered in previous publications concerning the application of amorphous carbon as an antireflective coating.

A general condition for minimal reflection using a single antireflective coating on a silicon solar cell is widely known and expressed by the equations,[29,30]

$$n_{film} = \sqrt{n_{air}n_{Si}} \quad \text{and} \quad t_{film} = \frac{\lambda_0}{4n_{film}}, \quad (1)$$

where n_{film}, n_{air}, and n_{Si} are the refractive indexes of the film, air and crystalline silicon, respectively, and t_{film} is the thickness of the film to supply a minimum reflectance in a specific wavelength, λ_0. This equation represents the well-known quarter-wavelength design for an antireflective coating. For silicon ($n \sim 4$, for the wavelength of 600 nm), this equation is satisfied when the refractive index of the antireflective coating is around 2. Under this condition, a thickness of about 75 nm is required in order to obtain a minimum reflectance at 600 nm, which is the wavelength with a high density of photons in the solar spectra[31] and with an elevated internal quantum efficiency of the silicon photovoltaic device under AM1.5 sunlight. Thus, in considering the use of amorphous carbon, one needs to develop films under the deposition condition and technique that supply a structure with a refractive index of 2.

If a broader region of low reflectance is desired, double-layers or even triple-layers are used.[32,33] The mathematical relations become more complex, but they can be solved to supply zero reflectance at 2 (for double-layers) or 3 (triple-layers) wavelengths. By using multiple layers one can broaden the region for very low reflectance, covering a wide range of the energy spectrum for a silicon solar cell ($\sim$ 300-1107 nm). The refractive index and the thickness of the films of a double-layer can be determined by the following relations,[33]

$$n_{top}^3 = n_{air}^2 \cdot n_{Si}; \ n_{bot}^3 = n_{air} \cdot n_{Si}^2 \quad \text{and} \quad t_{top} = \frac{\lambda_0}{4n_{top}}; \ t_{bot} = \frac{\lambda_0}{4n_{bot}}, \quad (2)$$

where n_{top} and n_{bot} represent the refractive index of the top and bottom layer, respectively, and t_{top} and t_{bot} represent the thickness of the top and bottom layer, respectively. Again, the quarter-wavelength design is adopted. Considering the refractive index of silicon ($n = 4$), the desirable refractive index of the films would be $n_{top} = 1.6$ and $n_{bot} = 2.5$.

II. EXPERIMENTAL

A. Amorphous carbon thin films

The PLC and DLC films were deposited by rf plasma enhanced chemical vapor deposition (rf-PECVD) using methane (CH_4, 99.99%) as the precursor gas. Table I summarizes the deposition parameters adopted. The system was pumped down to about 10^{-4} Pa prior deposition. The PLC films were deposited (on the anode) at a bias voltage (applied to the cathode) of -400 V and CH_4 pressure of 1 Pa at room temperature. The DLC films were deposited on the cathode, biased with -60 V, at 0.8 Pa of CH_4 at room temperature. These conditions were used in order to provide films with a high bandgap.

Tetrahedral amorphous carbon films were deposited at room temperature in a homemade FCVA system using a magnetic filter composed of a Cu solenoid bent into a quarter of a toroid shape and operating with a pulsed current of 190 A and 5 ns width at a frequency of 3 Hz. This system makes use of a solid graphite rod of 99.99% of purity as carbon source. The films were deposited on a double-side-polished silicon wafer for reflectance measurements, on Corning glass 7059 for transmission spectroscopy (for the determination of the optical bandgap and the refractive index), and on silicon solar cells for the evaluation of the actual improvement in the short-circuit current density due to the antireflective properties of the films. Further details about the properties of the films prepared by rf-PECVD and FCVA are described elsewhere.[6]

B. Hydrogenated amorphous silicon-carbon alloy

For the deposition of the a-SiC:H films, a mixture of argon (Ar) and hydrogen (H_2) was used to sputter a 3 in graphite target partially covered by small pieces of silicon. Different silicon/graphite area ratios were used to control the composition of the films. The other deposition

TABLE I. Deposition condition of the different forms of amorphous carbon films.

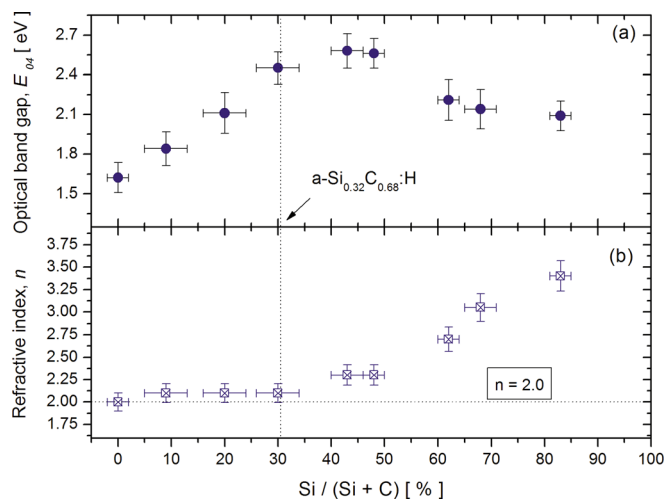| Amorphous carbon structure	PLC	DLC	ta-C
Deposition technique	rf-PECVD	rf-PECVD	FCVA
Electrode	anode	cathode	anode
Power conditions	-400 V	-60 V	190 A, $\sim$40 V,
	(applied to cathode)	(applied to cathode)	5ns, 3Hz
Precursor	CH_4	CH_4	graphite rod
Deposition pressure (Pa)	1.0	0.8	10^{-4}
Deposition temperature (°C)	room	room	room
Deposition rate (nm/min)	4.0	5.2	5.4

FIG. 1. (Color online) (a) Optical bandgap E_{04} (corresponding to the energy for which the absorption coefficient is 10^4 cm^{-1}), and (b) refractive index, at 632 nm, of silicon-carbon alloys deposited by sputtering Si/C composed targets, as a function of silicon concentration determined by RBS. The vertical dotted line indicates the composition adopted in this work, while the horizontal line indicates the desired refractive index.

parameters, i.e., the bias voltage of -1000 V, an Ar/H$_2$ ratio of 10:1, a total pressure of 0.8 Pa, and a deposition temperature of 220 °C were kept constant for all samples. Under this condition, a deposition rate of 3.1 nm/min was obtained. The composition of the films was determined by Rutherford backscattering spectroscopy (RBS), carried out using a He$^+$ beam with an energy of 2.2 MeV.

The bandgap and the refractive index dependence on the Si/C composition of the amorphous alloy are shown in Fig. 1. Since we are considering the use of silicon-carbon alloys as antireflective coatings, a composition responsible for high bandgap and a refractive index of about 2 was chosen, as displayed in Fig. 1. Thus, we adopted the a-Si$_{0.32}$C$_{0.78}$:H alloy composition, since the silicon to carbon stoichiometric ratio of 1:1 (50% silicon in Fig. 1) has a high refractive index (~ 2.25), which is not well-suited as a single antireflective coating on a silicon solar cell.

C. Antireflective coating on solar cells

Conventional p-n homojunction silicon solar cells were fabricated using a p-type (1 Ω cm) Cz-silicon, through the thermal diffusion of phosphorous (using the POCl$_3$ dopant carrier), and an aluminum back surface field, followed by evaporation of Ti/Pd/Ag contacts. Each antireflection layer was deposited on the solar cell fabricated on a plain surface and on a texturized (pyramidal) structure obtained through the anisotropic reaction of the (100) silicon with NaOH water solution. Double-layer antireflective coatings were also prepared using a combination of amorphous carbon and magnesium fluoride (MgF$_2$), which was thermally evaporated. For the sake of comparison, tin dioxide (SnO$_2$), a well-known transparent conductor oxide used for antireflective coatings, was deposited by spray pyrolysis at 250 °C.

Reflectance and transmittance spectroscopy in visible and near infrared ranges were performed in a Perkin-Elmer Lambda 9 spectrophotometer. The package PUMA[34] (appro-

priated for very thin films) was used to recover the refractive index and the extinction coefficient, from which the absorption coefficient and bandgap was obtained. The existence of a high density of localized and extended states between the valence and conduction bands in amorphous semiconductors makes it difficult to establish a value for the material bandgap. There are several definitions of the bandgap for such types of materials based on different electronic structures and optical parameters. In this work we make use of the E_{04}, which is the energy for which the absorption coefficient is 10^4 cm^{-1}. This definition has been used for amorphous semiconductors and is usually higher than Tauc's bandgap. The current versus voltage characteristics of the solar cells (before and after the deposition of the antireflective coating) were obtained using a Keithley 238 High-Current Source Measure Unit under 100 W/cm^2 AM1.5 light illumination. The thickness of the antireflective coating was determined with a Dektak Veeco Profilometer, model 150.

III. RESULTS

A. Single antireflective coating

The important optical parameters concerning the use of antireflective coatings are the refractive index, optical bandgap, and the absorption coefficient. High conductivity is desirable, but not fundamentally necessary, since an appropriated metallic contact grid can overcome the problems related to the series resistance of the phosphorous-doped layer. Table II summarizes the results for the optical bandgap (E_{04}) and refractive index (n) at ~ 632 nm wavelength for the materials studied as antireflective coatings. This wavelength is commonly used in measurements performed using the He-Ne laser.

One can observe that the refractive index of some of the carbon materials developed in this work (PLC and ta-C) is not well suited for use as a single antireflective coating on a silicon solar cell, since it is higher than 2.0. The effect of using a refractive index other than 2 can be evaluated using integrated reflectance spectroscopy, as shown in Fig. 2 (it is worth mentioning that a result similar to that Fig. 2(a) has already been shown in Ref. 6 by Oliveira *et al.*). The thickness of all of the films shown in Fig. 2 was chosen to provide a minimum reflectance for radiation with a wavelength of about 600 nm. One can observe that the minimum reflectance for SnO$_2$ ($n = 2$) is close to zero. On the contrary, the minimum reflectance increases for DLC ($n = 2.2$), PLC ($n = 2.4$), and ta-C ($n = 2.6$) to 2.2, 4.9, and 7.8%, respectively. As for the silicon-carbon alloy, Fig. 2(b), the reflectance is comparable to that of SnO$_2$, as expected, once both have the same refractive index.

TABLE II. Optical properties of different carbon structure (DLC, PLC, and ta-C), a-SiC:H, SnO$_2$, and MgF$_2$.

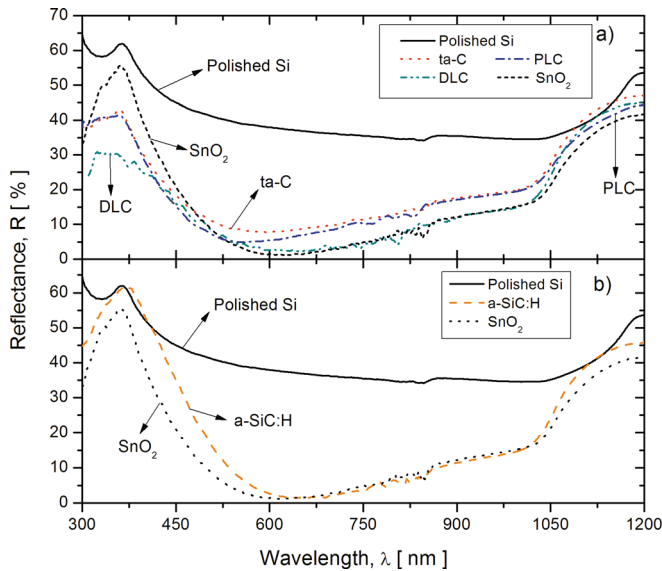|	DLC	PLC	ta-C	a-SiC:H	SnO$_2$	MgF$_2$
n ($\sim$632 nm)	2.2 ± 0.2	2.4 ± 0.2	2.6 ± 0.2	2.1 ± 0.2	2.0 ± 0.2	1.4 ± 0.3
E_{04} (eV)	1.7 ± 0.2	2.8 ± 0.1	1.6 ± 0.2	2.6 ± 0.2	3.0 ± 0.3	$\sim 5.0^a$

^{a}Data extracted from Ref. 35.

FIG. 2. (Color online) Integrated reflectance spectra for different types of carbon structures: (a) amorphous carbon (DLC, PLC, and ta-C), and (b) a-Si$_{0.32}$C$_{0.78}$:H alloy, compared with the reflectance of conventional SnO$_2$ deposited by spray pyrolysis and uncoated polished silicon.

B. Double layer antireflective coating

In Sec. III A, we observe that the refractive index of ta-C and PLC films with high bandgap do not match the appropriate value for a single antireflective coating ($n = 2$). In this section we explore the possibility of using these materials in double-layer antireflective coatings. Figure 3 shows the reflectance spectra of the PLC/MgF$_2$ and ta-C/MgF$_2$ double-layers, compared to the conventional ZnS/MgF$_2$ antireflective coating. One can observe that low levels of reflectance were achieved for both structures in a broad wavelength range. Thus, considering the reflectance spectra, ta-C/MgF$_2$ or PLC/MgF$_2$ double-layers are equivalent to the conventional ZnS/MgF$_2$ structure.
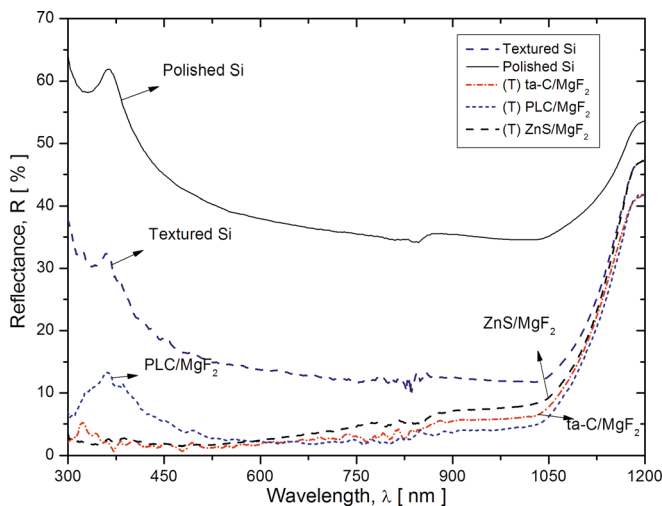

FIG. 3. (Color online) Integrated reflectance spectra for PLC/MgF$_2$ and ta-C/MgF2 double-layer antireflective coatings on silicon compared with a conventional ZnS/MgF2 double-layer. The reflectance for textured silicon is also shown for comparison.
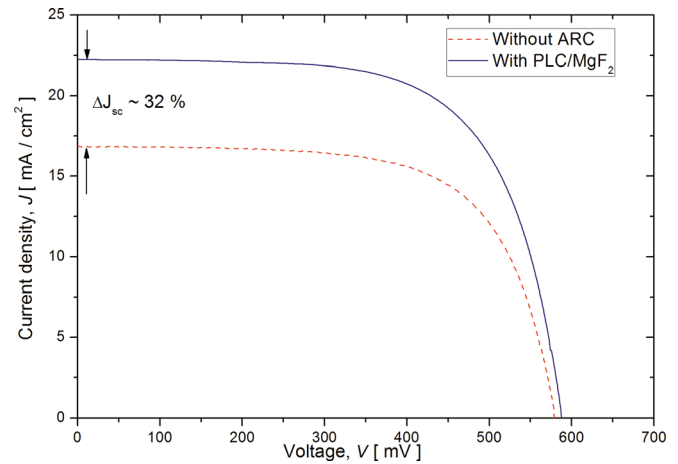

FIG. 4. (Color online) Current density vs voltage of an illuminated silicon solar cell with and without a double-layer PLC/MgF$_2$ antireflective coating, with a thickness of 59 ± 3 and 98 ± 5 nm, respectively.

C. Solar cells with single-layer and double-layer antireflective coatings

Figure 4 displays the current density versus voltage characteristic of a solar cell before and after the deposition of a PLC/MgF$_2$ double-layer antireflective coating. A significant increase of about 32% in the short-circuit current density is observed. In the remainder of this paper we will address only the effect on the short-circuit current density as it reflects the actual efficiency of the antireflective coating, since it is directly related to the electron-hole pair generation, which in turn depends on the number of photons absorbed by the solar cell.

Table III displays the best results for several combinations of single and double-layer antireflective coatings used on p-n junction silicon solar cells. As can be observed, all carbon-based structures investigated here work as antireflective coatings, but with varying efficiency. The SnO$_2$ promotes an increase in the short-circuit current density of about 37%, as expected for a good antireflective coating

TABLE III. Percentage increase in the short-circuit current density (ΔJ_{sc}) of a variety of combinations of carbon-based materials in the silicon solar cell, including single- and double-layer antireflective coatings on polished and on texturized silicon (Text). The data in the brackets represents the total increase in the short-circuit current density when the texturization is taken into account.

Structure	Antireflective coating	ΔJ_{sc} (%)
	DLC	22.6
	PLC	23.8
Single layer	ta-C	13.0
	a-Si$_{0.32}$C$_{0.68}$:H	25.8
	SnO$_2$	37.0
	PLC/MgF$_2$	31.4
Double-layer	ta-C/MgF$_2$	21.3
	Text	30.0
Texturized	Text/DLC	3.4 (34)
+ single or double	Text/PLC	7.6 (40)
layers	Text/PLC/MgF$_2$	10.8 (44)
	Text/ta-C/MgF$_2$	8.2 (41)

since it has the appropriate refractive index (2.0) and a high bandgap (3.0 eV). However, the increase in short-circuit current density for DLC, PLC, and ta-C are smaller than for SnO$_2$. The reasons for that are: (a) DLC has a refractive index close to that of SnO$_2$ but a lower bandgap ($E_{04} = 1.7$ eV); (b) ta-C films have a high refractive index (2.6) and a low bandgap (1.6 eV); and (c) PLC has a high bandgap (2.8 eV) and a high refractive index (2.4). On the contrary, when we used PLC on a double-layer antireflective coating with MgF$_2$, we obtained a high short-circuit current density. This is explained by the fact that the index of refraction of PLC (2.4) is more appropriate for a double-layer antireflective coating, as can be inferred from Eq. 2, than for a single layer. For the same reason, ta-C/MgF$_2$ also improves the short-circuit current compared to the use of a single antireflective coating of ta-C. In this case, the refractive index is appropriate, however the bandgap of the ta-C is not high enough. Table III also shows that the use of the PLC, PLC/MgF$_2$, and ta-C/MgF$_2$ structures promote an additional increase in textured silicon solar cells. As is shown in Fig. 3, the use of texturization can reduce the reflectance (at about 600 nm) from 37% to about 13%. Thus, a total increase in the short-circuit current density higher than 40% (data in brackets in Table III) is achieved when using a combination of texturization and the structures mentioned in the preceding text.

None of the single carbon-based antireflective coatings (Table III) promoted an increase in the short-circuit current comparable to that obtained with SnO$_2$. The highest improvement obtained here was achieved by using the PLC/MgF$_2$ double-layer antireflective coatings (31.4%) and the texturized-Si/PLC/MgF$_2$ structure (44%).

IV. DISCUSSION

A. Drawbacks of amorphous carbon as antireflective coatings

The use of amorphous carbon as an antireflective coating has been reported in several papers.[1–9] Alaluf *et al.*,[4] Choi *et al.*,[5] and Pern *et al.*[9] achieved an increase in the short-circuit current density in the 4–20% range. For similar structures (DLC films) reported in those references, we obtained a 22.6% increase, probably because the bandgap of our material (1.7 eV) is higher. Using tetrahedral-like (ta-C) and polymeric-like (PLC) structures instead, we achieved 13.0 and 23.8%, respectively. In a previous work, we obtained a 33.7% increase using PLC films.[6] There are some papers reporting improvement higher than those previously mentioned.[1,3] However, the materials used in those works are not pure amorphous carbon, but amorphous carbon doped with either silicon or nitrogen. These elements may help to open the bandgap and to change the refractive index to better attend the condition for single- and double-layer antireflective coatings.

The aforementioned improvements in the short-circuit current are still below the values one can obtain using conventional antireflective coatings, such as SnO$_2$, which promotes an increase of about 37% (Table III). The main drawbacks of non-hydrogenated amorphous carbon (a-C) as
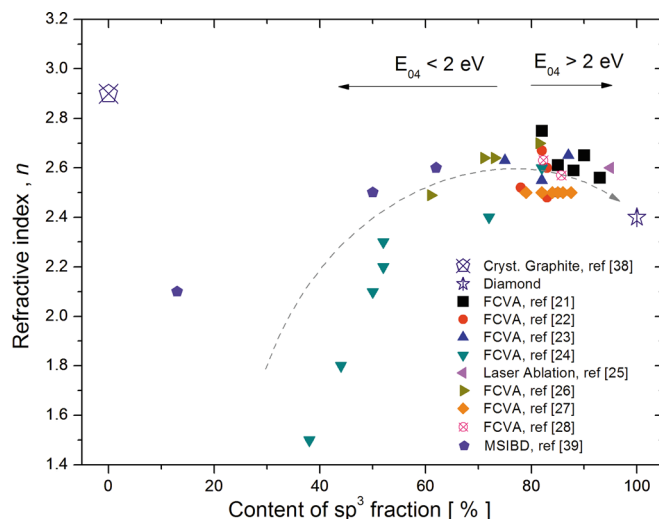

FIG. 5. (Color online) Variation of the refractive index (at approximately 632 nm) of unhydrogenated amorphous carbon films (a-C) as a function of the sp^3 concentration.

an antireflective coating are related to their refractive index, bandgap and stress, as discussed next.

Figure 5 displays several results reported in the literature for the refractive index for non-hydrogenated amorphous carbon (a-C) as a function of the concentration of sp^3 carbon atoms.[21–28,38,39] These films are usually deposited by sputtering, laser ablation, or FCVA. However, the bandgap of the films with sp^3 concentration below 70–80% is smaller than 2.0 eV, which is not suitable for antireflective coatings. It has been observed that the bandgap of amorphous carbon strongly depends upon the content of sp^2 atoms, and is directly proportional to the sp^3 concentration for films with a high concentration of sp^3 atoms.[10,37] It is well known that the π bonding and antibonding states (π-π*), of the sp^2 sites, are located between the σ bonding and antibonding states (σ-σ*),[36] lowering the effective optical bandgap of amorphous carbon. A bandgap higher than 2.0 eV is achieved only in films with a very high sp^3 fraction (>70–80%). Those films are known in the literature as tetrahedral amorphous carbon (ta-C).

The increase in sp^3 sites opens the bandgap of a-C films (Fig. 5), however, it is accompanied by an increase in the refractive index, approaching that of diamond (2.4), being even higher in the range of 60–95% sp^3 concentration. Thus, ta-C films are not suited for single antireflective coatings in crystalline solar cells. In addition, films with a high sp^3 fraction are extremely compressively stressed, in the 5–15 GPa range. These values of mechanical stress are so high that films thicker than 70–80 nm (typical for an antireflective coating) are very unstable, easily peeling off from the substrate.

One way to circumvent the problem of the high refractive index of a-C films with high sp^3 concentration would be the use of hydrogenated amorphous carbon (a-C:H). Figure 6 displays several results reported in the literature[38,45–47] for the refractive index (at about 632 nm) for a-C:H films prepared by different techniques. Films with an intermediate concentration of sp^3 sites are usually deposited by PECVD[10,40] on the biased electrode (cathode), and is usually
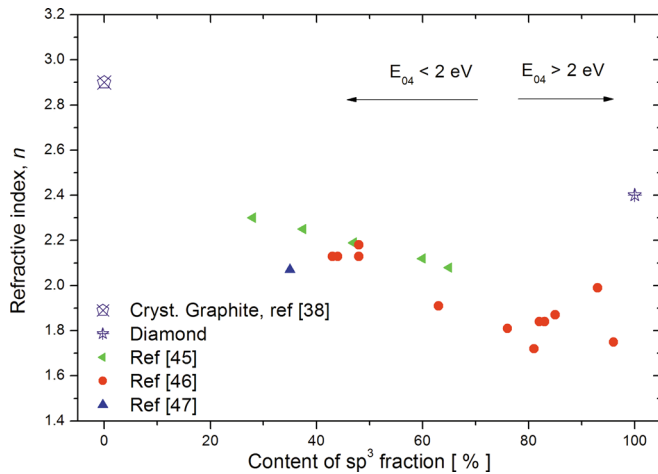
FIG. 6. (Color online) Variation of the refractive index (at approximately 632 nm) of hydrogenated amorphous carbon films (a-C) as a function of the sp^3 concentration.

referred to as a DLC. Films with a concentration of sp^3 C-C bonding higher than 50% are usually deposited by FCVA and are known as hydrogenated tetrahedral amorphous carbon (ta-C:H). Similar to its nonhydrogenated counterpart (ta-C), only films with a high sp^3 fraction (>70–80%) have bandgaps higher than 2 eV. Depending upon the deposition condition, it can be prepared with a refractive index of 2 (Fig. 6). However, the stress of ta-C:H films is also very high.

The PLC films also have a very high content of sp^3 sites, high bandgap, and low stress, but a very high concentration of hydrogen (40–60%), which makes this material very soft so it does not work as a protective coating, an important requirement for an antireflective layer.

Figure 6 suggests that the refractive index of amorphous carbon is small for films with a high concentration of sp^3 sites. However, there are several works reporting the refractive index for polymeric films (very high concentration of sp^3 sites) in the 1.6–2.7 range,[41,42–44] but they do not supply the sp^3 fraction.

In this work we did not investigate the use of the ta-C:H film, however, it appears that it would be more appropriate for a single antireflective coating on silicon solar cells than ta-C films.

The use of double-layer antireflective coatings can overcome the problem of the refractive index of amorphous carbon. In our work, the use of ta-C or PLC works reasonably well (see Table III). The bandgap of the ta-C film developed here was only 1.6 eV, which explains the low improvement in the short-circuit current density. Litovchenko[1] and Klyui et al.[3] tested double-layers composed only of DLC films, but used nitrogen to open the bandgap (a-C:H:N) and to obtain different films with different refractive indexes. They reported an impressive increase of 36.7% in the short-circuit current density.

B. The effect of the optical bandgap

Figure 7 displays a histogram of the relative improvement of the short-circuit current density obtained for the

films developed in this work and the theoretical values that could be achieved considering the experimental integrated reflectance displayed in Figs. 2 and 3. In this calculation, we considered the antireflective coating with 100% transmittance (transparent films) and internal quantum efficiency of the solar cell equal to 1. The total short-circuit current density was then obtained through the Eqs. (3) and (4),

$$J_{sc} = \int_{\lambda_1}^{\lambda_2} I_S \cdot SR \, d\lambda, \tag{3}$$

$$SR = \frac{(1-R) \cdot IQE}{hc/e\lambda}, \tag{4}$$

where I_s is the AM1.5 solar irradiance,[31] SR is the spectral response, λ_1 and λ_2 are the wavelength limits, 300 and 1107 nm, respectively (which is the range of interest for the silicon solar cell), R is the reflectance (Figs. 2 and 3), h is Planck's constant, c is the velocity of light, and e is the electron charge.

As can be observed in Fig. 7, we had obtained an improvement in the short-circuit current density very close to the one expected for the texturized surface and the SnO$_2$ antireflective layer. However, the other materials did not supply the expected current density if one considers only the total reflectance (Figs. 2 and 3). The absorbance coefficient of the films also needs to be considered along with the solar spectrum, as shown in Fig. 8. One can clearly observe that part of the spectrum has been strongly absorbed by the DLC and ta-C films. Thus, an improvement in the J_{sc} cannot reach a value above 30% using these materials in single- or double-layers (Table III).

Figure 7 also shows the ideal theoretical limit of improvement in the short-circuit current density and it can
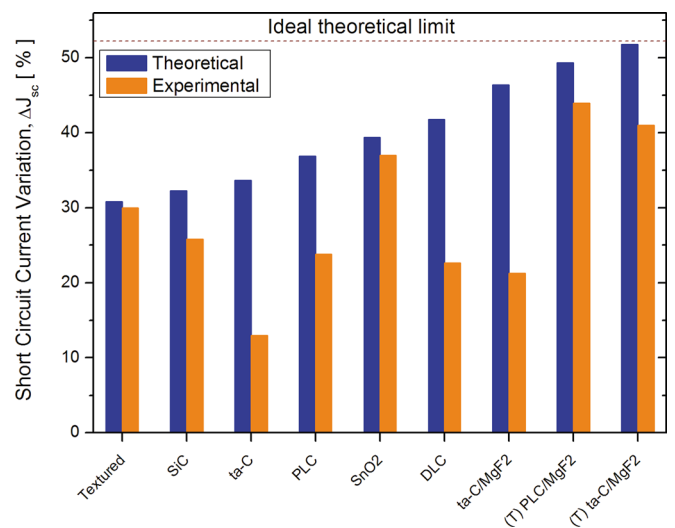

FIG. 7. (Color online) Improvement in the short-circuit current density for some antireflective films developed here (right column), compared with the expected improvement using the experimental reflectance spectra of Figs. 2 and 3, but considering the films to be 100% transparent and the internal quantum efficiency of the solar cells equal to 1 (left column). The "ideal theoretical limit" was calculated considering the reflectance equal to zero in the whole range of the wavelength.

almost be achieved if one uses a texturized silicon surface and a very transparent double-layer. Thus, the use of an additional layer (triple-layer) to improve the short-circuit current of the silicon solar cell does not cause any significant improvement when using texturization.

The effect of increasing the optical gap in the short-circuit current density can be evaluated in Fig. 9, which shows a relative increase of the short-circuit current density with increasing bandgap. This figure shows the importance of having materials with a very high bandgap in order to obtain a high short-circuit current in solar cells. For amorphous carbon films, this condition is met when using films with a high density of sp^3 bonds, such as the PLC films. The ta-C films can also meet this condition if prepared in a more sophisticated FCVA system, using an S-bend magnetic filter, for instance.[48]

C. Hydrogenated silicon-carbon alloy as antireflective coating

Since a-C and a-C:H do not possess the main properties required for a good antireflective coating, one approach would be the use of a carbon alloy. A Silicon-carbon alloy is a good candidate if one considers the use of abundant and environmentally friendly materials. The use of a-SiC:H in this work promoted an increase of about 26% in the short-circuit current density (Table III). Its absorption coefficient is reasonably better than DLC and ta-C (Fig. 8), and is well-suited for antireflective coatings on crystalline silicon solar cells.

Stapinski and Swatowska[49] developed a silicon-carbon antireflective coating of $SiH_4 + CH_4$ over multicrystalline silicon solar cells by PECVD and obtained an increase in the short-circuit current of 24.7%. Klyui *et al.*[3] used ion-plasma sputtering of a SiC target, in an argon-hydrogen atmosphere, and obtained an increase in the short-circuit current of 29.7%. Buršíková *et al.*[2] also obtained about a 30% increase in the short-circuit current. Those results are similar to ours, confirming the good antireflective performance of the
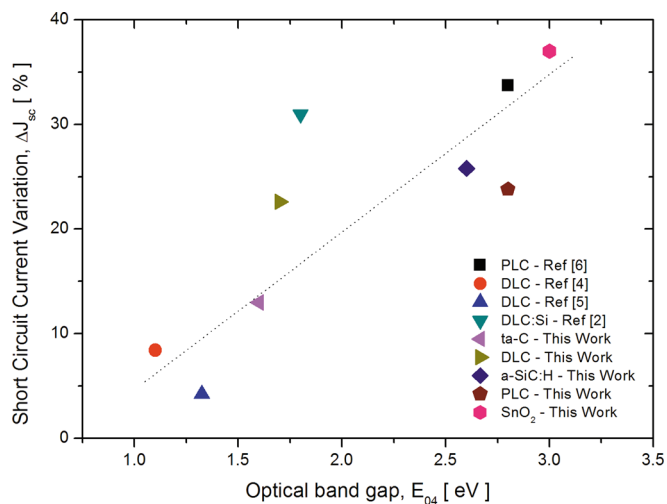
FIG. 9. (Color online) Increase in the short-circuit current of crystalline silicon solar cells due to the use of an antireflective coating of a carbon-based material, compared with a conventional SnO_2 antireflective coating.

a-Si_xC_{1-x}:H films along with the benefits of being environmentally sound, hard, stable, with good adherence to silicon, and chemically inert. In addition, the electrical conductivity of silicon-carbon films can be greatly improved by doping, which is another limitation of pure carbon.

V. CONCLUSION

Amorphous carbon films with different structures were investigated as potential candidates for antireflective coatings on silicon solar cells. Diamond-like carbon (DLC) and polymeric-like carbon (PLC) were prepared by rf-PECVD. Tetrahedral-like carbon (ta-C) was prepared by FCVA. Single- and double-layer antireflective coatings were realized on polished and on texturized silicon solar cells. The results were compared with conventional SnO_2 deposited by spray pyrolysis and ZnS/MgF_2. The main findings of this work can be summarized in the following:

(1) Diamond-like carbon (DLC) can be prepared with a refractive index of 2, high hardness, and chemically inertness. However, the bandgap is usually smaller than 2 eV due to the relatively high density of sp^2 sites. Thus, it is not a good candidate for an antireflective coating for silicon solar cells.

(2) Polymeric-like carbon (PLC) can be prepared with a refractive index of 2, high bandgap ($\sim$3 eV), chemical inertness, but is a very soft material and thus is not well-suited for the mechanical protection of the device.

(3) Nonhydrogenated tetrahedral amorphous carbon (ta-C), can be prepared with a high bandgap (2.5 eV), chemical inertness, high hardness, but the refractive index is higher than 2.4. Thus, it is not appropriate for a single antireflective coating, but can be used in a double-layer antireflective coating, for instance, using the ta-C/MgF_2 structure, which shows an improvement of about 21.3% and a total of 44% in conjunction with the textured surface. However, the film is highly stressed (5–15 GPa) and can easily peel off the substrate.
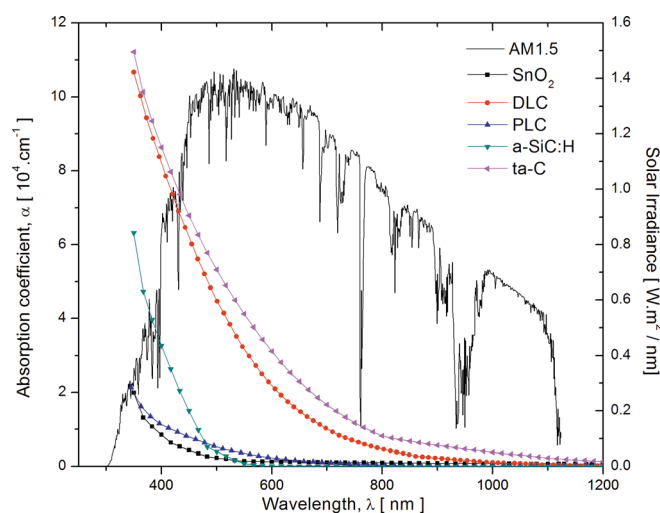

FIG. 8. (Color online) Absorption coefficient of different structures of amorphous carbon (PLC, DLC, and ta-C) and a silicon-carbon alloy as a function of the wavelength, compared with the AM1.5 solar irradiance spectrum.

(4) Hydrogenated tetrahedral amorphous carbon (ta-C:H) can be prepared with a refractive index of 2, it is also chemically inert, very hard, and may have a high bandgap. However, similarly to ta-C films, ta-C:H films are also highly stressed.

(5) Considering carbon-based materials, silicon-carbon alloy (a-Si$_x$C$_{1-x}$:H) is a good choice for an antireflective coating on a silicon solar cell. It has a high bandgap, is hard, chemically inert, can be doped, and may have a refractive index of about 2. In addition, these alloys are composed of abundant and environmentally sound elements.

ACKNOWLEDGMENTS

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