AMORPHOUS CARBON AS ANTIREFLECTIVE COATING FOR SOLAR CELLS

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ABSTRACT: Different structures of hydrogenated amorphous carbon (a-C:H) are used as antireflective coating (ARC) on crystalline (polished and textured) silicon solar cells. Conventional p-n junction solar cells were fabricated following standard phosphorus diffusion procedure. Polymeric-like carbon (PLC) was deposited on the anode of a plasma enhanced chemical vapor deposition (PECVD) system, while diamond-like carbon (DLC) were deposited on the cathode electrode. Integrated visible and near-infrared reflectance spectroscopy was used for determining the appropriated thickness to achieve the smallest reflectance at 600 nm wavelength and to determine the index of refraction of the ARC. SnO₂ antireflective coating was also used for comparison. It was observed that the reduction on the reflectivity of the amorphous carbon film/silicon surface is comparable to that obtained by SnO₂, showing that amorphous carbon can be used as antireflective coating.

Keywords: Amorphous Carbon, Antireflective Coating, Solar Cell.

1 INTRODUCTION

Amorphous carbon structures, such as diamond-like (DLC) and polymeric-like carbon (PLC), have interesting and very useful properties. Physical phenomena involving optical and mechanical characteristics can be explored with these materials [1]. The use of amorphous carbon as antireflective coating (ARC) in solar cells improves the solar cell efficiency due to an improvement in the current density [2, 3, 4]. The materials used for that purpose need to accomplish some conditions: 1) be transparent in the region of interest for solar cell, and 2) the index of refraction of the film, n_{film} , and substrate, need to satisfy the relation n_{substrate}, $n_{film} = \sqrt{n_{substrate}}$ [5]. For crystalline silicon solar cell, $n_{substrate} = 4$. Thus, the appropriated index of refraction for a single antireflective coating requires $n_{film} = 2$.

A large variety of materials has been used as ARC on solar cells such as ITO, SnO₂, SiO₂, double layer of ZnS/MgF₂, among others. Some of these compounds use elements that face disposable problems, such as indium, tin, magnesium and sulfur, which cause environment concern in large scale production of solar cells. In this sense, amorphous carbon could be a very good choice since it can be produced by simple technique, hard, chemically inert, low friction coefficient and is environmentally sound. In this work, we investigate the use of different structures of amorphous carbon, i.e, polymeric-like and diamond-like carbon on polished and textured crystalline silicon solar cell.

2 EXPERIMENTAL

2.1 Deposition conditions

Amorphous hydrogenated carbon (a-C:H) films were deposited by the rf plasma enhanced chemical vapor deposition (PECVD) method. A 13.56 MHz Dressler Cesar 1310 RF power generator was used to decompose a methane (CH₄) atmosphere. DLC films were obtained in films deposited on the cathode electrode at a bias of 90V. The PLC films, on the other hand, were obtained on the anode electrode. A 400 V bias voltage were adopted on the cathode, which represents a bias voltage on the anode in the 20-30 eV range. Table I summarizes the deposition condition of the a-C:H films presented in this paper.

| Table I: Deposition condi | tion of the am | orphous films |
|--|----------------|---------------|
| deposited on the anode (PI PECVD system | LC) and cathoo | te (DLC) of a |
| | DI C | DLC |

| | PLC | DLC |
|----------------------------|------------------|---------|
| Deposition Pressure [mbar] | 10 ⁻² | 10-2 |
| Electrode | Anode | Cathode |
| Bias on the cathode[V] | 400 | 90 |
| Temperature | room | room |
| Deposition Time [min] | | |
| Sample #1 | 25 | 17 |
| Sample #2 | 23 | 15 |
| Sample #3 | 22 | 12 |
| Sample #4 | 21 | - |

2.2 Solar cell fabrication

Conventional p-n junction crystalline (100) silicon solar cells were made using the procedure reported elsewhere [6]. In short, phosphorus diffusion was performed at 900°C, providing a sheet resistance of about 40 Ω_{\Box} . Aluminum back surface field was realized on the back surface. Ti-Pd-Ag were thermally evaporated on both sides. The shadow technique was adopted to obtain the front grid. Ordinary (92-95%) chemical solvents and acids were used, which is responsible for the relatively low efficiency obtained for the solar cells present here. However, the conclusion of the paper is not affect by this fact.

Current versus voltage curves were obtained in a home-made solar simulator. The system is composed by an electric power supply that feeds a tungsten-halogen lamp calibrated for the AM1 spectrum. A Keithley 238 High Current Source Measure Unit is used to generate the IxV curves, which are further computer analyzed.

2.3 Film characterization

Transmission and integrated reflection were measured using a Perkin-Elmer model lambda 9 UV/VIS/NRI (ultraviolet/visible/near infrared) spectrophotometer. Usually, the thickness and index of refraction of thin films are extracted from the interference fringe obtained by transmission spectroscopy. However, this procedure requires relatively thick films (about 1 μ m). In this work, where the antireflective coating is less than 0.1 μ m thick, we adopted the integrated reflectance curves to obtain the index of refraction in the range of energy of interest for Si crystalline solar cell (around 600 nm, which correspond the wavelength for maximum photon density in the AM1 solar spectrum) and the thickness of the films. This can be done using the minimal reflectance to obtain the index of refraction of the films, through equation,

$$n_{film} = 2 \cdot \left(\frac{(1 + \sqrt{R_{MIN}})}{(1 - \sqrt{R_{MIN}})} \right)^{\frac{1}{2}}$$
(2)

and its corresponding wavelength value to obtain the thickness of the films [7],

$$d = \frac{\lambda_{MIN}}{n_{film}} \tag{3}$$

3 RESULTS AND DISCUSSION

3.1 Optical properties of the ARC

Integrated reflectance spectra of different types of carbon structures are compared in Figs. 1 and 2 as a function of the deposition time (see Table I). The deposition time was altered to change the optical thickness of the films seeking for a minimal reflectance around 600 nm.



Figure 1 - Reflectance spectra of PLC films on crystalline silicon as a function of the deposition time (see Table I)

As can be observed, the amorphous carbon antireflective coating works reasonable well. A minimum reflectance of 6.8% and 2.2% were obtained for polymeric- and diamond-like carbon films, respectively. This reduction in reflectance is higher than that obtained by chemical texturization of the (100) silicon surface, which reflects about 11%.



Figure 2 - Reflectance spectra of DLC films on crystalline silicon as a function of the deposition time (see Table I)

Figure 3 displays the best results found in Figs. 1 and 2, compared with a SnO_2 antireflective coating, deposited using the spray technique [8]. As can be observed, DLC films seem to be as good as SnO_2 and PLC films are not much different. The difference in the minimal reflectance of the amorphous carbon ARC is related mainly to the mismatch in the index of refraction of the films. Tables II and III present these parameters obtained through the procedure described in the experimental section, equation 1 and 2, using data of Figs. 1 and 2.



Figure 3 - Reflectance spectra for different antireflective coating on crystalline silicon.

 Table II: Optical properties of polymeric-like carbon (PLC)

| | #1 | #2 | #3 | #4 |
|--------------------|---------------|-------------|-------------|---------|
| Minimal | | | | |
| reflectance [%] | 11.7 | 11.8 | 8.9 | 6.8 |
| Wavelength (minima | l | | | |
| reflectance) [nm] | 775 | 592 | 564 | 643 |
| Thickness [nm] | 69±8 | 51±6 | 52±6 | 61±8 |
| Index of | | | | |
| refraction | 2.8 ± 0.3 | 2.9 ± 0.3 | 2.7 ± 0.3 | 2.6±0.3 |

| | #1 | #2 | #3 |
|-------------------------|---------------|---------------|---------------|
| Minimal reflectance [%] | 2.25 | 2.19 | 2.36 |
| Wavelength of minimal | | | |
| reflectance [nm] | 741 | 690 | 629 |
| Thickness [nm] | 81±4 | 74±4 | 66±3 |
| Index of | | | |
| refraction | 2.3 ± 0.5 | 2.3 ± 0.5 | 2.4 ± 0.5 |

 Table III: Optical properties of diamond-like carbon (DLC)

The average index of refraction of the films deposited on the cathode (DLC) is about 2.3 ± 0.5 and about 2.7 ± 0.3 for the films deposited on the anode (PLC). Since those values are higher than 2 (which would be the ideal value for ARC in c-Si) the minimum reflectance can not be reduced to zero. The DLC films are the ones with index of refraction closer to 2 (within experimental error). This explains why the reflectance with DLC-ACR is smaller than with PLC-ARC.

3.2 Solar cell

The DLC and PLC films showed properties that make possible their use as ARC in c-Si solar cell in spite of the value of the index of refraction – a little bit over the ideal value, 2. These materials were deposited over crystalline silicon solar cells as antireflective coating. For PLC we use the same conditions of sample number 4 and for DLC we repeated the conditions of sample 3. The photovoltaic parameters of the cells are showed in Table IV and compared with those obtained using SnO_2 ARC as well.

 Table IV: Photovoltaic parameters of solar cells with amorphous carbon and tin dioxide as ARC

| | PLC | DLC | SnO_2 |
|---------------------------------------|--------------|--------------|--------------|
| | Before After | Before After | Before After |
| V _{max} [mV] | 423 433 | 396 394 | 376 366 |
| I _{max} [mA] | 67.0 81.3 | 19.9 27.8 | 93.0 97.3 |
| V _{oc} [mV] | 598 598 | 561 558 | 572 559 |
| J _{sc} [mA/cm ²] | 25.5 34.1 | 21.0 25.6 | 21.0 26.8 |
| A [cm ²] | 3.2 3.0 | 1.2 1.2 | 6.2 3.8 |
| FF [%] | 57.1 57.5 | 55.3 63.4 | 46.5 51.6 |
| η [%] | 8.7 11.7 | 6.5 9.0 | 5.6 7.7 |

Table IV shows an increase in the short-circuit current density of 33 % for the cell with PLC as ARC and 22 % for DLC. The increase in efficiency, on the other hand was about 34 % and 38 % for PLC and DLC respectively. This difference in efficiency is associated with an improvement of the fill factor for the DLC films, which must not be associated with the antireflective coating, but a reduction in the series resistance instead.

It can be noted that the improvement in efficiency are mainly due to the improvement in the short-circuit current. In fact, the main effect of the ARC is to increase the short-circuit current due to a reduction on the reflectance. We did not observe an increase in the open circuit voltage as reported by Alaluf *et al* [3]. It is possible that other effects might contribute to the increase in the open circuit voltage, such as a passivation effect of the silicon surface. An increase in fill factor is also possible due to a reduction of the metallic contact resistance through thermal annealing during the deposition process.

The optical band gap for PLC films, obtained through

the PUMA program [9] was $E_{04} = \sim 2.9$ eV and for DLC film $E_{04} = \sim 1,6$ eV. These values show that polymericlike carbon is more appropriated for ARC since they are more transparent. However, even though the band-gap of the DLC films is not high, it is good enough to allow the visible light to be transmitted to the p-n junction, since the films is very thin (less than 0.1 µm) and the absorption edge is not abrupt, allowing photon to be transmitted at energy higher than E_{04} . However, this is probably the reason the increase in the short-circuit current was not as high as that obtained with PLC, which band gap is much higher.



Figure 4 – J x V curve of solar cells with DLC (A) and PLC (B) antireflective coating

The density of current versus voltage curves for the solar cell displayed in Table IV, using PLC and DLC antireflective coating, are shown in Fig. 4. The results for texturized cells are presented in Table V and Fig. 5.

 Table V: Photovoltaic parameters of texturized silicon solar cell with amorphous carbon as ARC

| | PLC | | DLC | |
|---------------------------------------|--------|-------|--------|-------|
| | Before | After | Before | After |
| V _{max} [mV] | 369 | 379 | 379 | 380 |
| I _{max} [mA] | 140.0 | 88.0 | 30.4 | 30.6 |
| V _{oc} [mV] | 599 | 589 | 552 | 551 |
| J _{sc} [mA/cm ²] | 32.8 | 35,3 | 29.4 | 30.1 |
| A [cm ²] | 6.2 | 3.2 | 1.4 | 1.4 |
| FF [%] | 42.0 | 59.8 | 59.2 | 48.6 |
| η [%] | 8.2 1 | 0.3 | 8.0 | 8.1 |



Figure 5 – J x V curves for texturized silicon solar cells with DLC (A) and PLC (B) antireflective coating

The improvement of the photovoltaic parameters for the textured silicon solar cell is much smaller then that obtained for non-textured cells. This is expected, since the textured structure already works as an antireflective surface, reducing the reflectance to about 11 %. As a consequence, a much less improvement is observed. The additional enhancement in the short-circuit current density with the PLC- and DLC-ACR are 7.6 % and 2.5 %, respectively.

The enhancement in the short-circuit current for PLC- and DLC-ARC are comparable to that obtained for SnO₂, within experimental error. This behavior shows that amorphous carbon, with both polymeric- and diamond-like structures, can be used as antireflective coating. Since polymeric films are soft, one wants to use DLC films instead, which is much harder than silicon, is chemically inert and has low friction coefficient. For that purpose, DLC films with higher band gap would work even better. This can be achieved under appropriated condition.

4 CONCLUSIONS

Different structures of amorphous carbon films were used as antireflective coating in crystalline silicon solar cells. The high index of refraction of the PLC films is the main responsable for the relatively high total reflectance as compared with SnO₂. The DLC films, on the other hand, has a lower total reflectance, but its smaller band gap accounts for some light absorption in the solar energy spectrum. In spite of that, an increase in the shortcircuit current comparable to that obtained for SnO₂ was also obtained with DLC- and PLC-ARC. Thus, one concludes that amorphous carbon can be used as antirefletice coating on crystaline silicon solar cell. In addition to the good properties of these films, such as chemical inertness, low friction coeficient and high hardness, it is also environmentaly sound.

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REFERENCES

- J. Robertson, Materials Science and Engineering R. 37 (2002) 129-281.
- [2] N.I. Klyui, V.G. Litovchenko, A.G. Rozhin, V.N. Dikusha, M. Kittler, W. Seifert, Solar Energy Materials & Solar Cells. 72 (2002) 597-603.
- [3] M. Alaluf, J. Appelbaum, L. Klibanov, D. Brinker, D. Scheiman, N. Croitoru, Thin Solid Films. 256 (1995) 1-3.
- [4] V. Buršíková, P. Sládek, P. St'ahel, L. Zajíčková, Journal of Non-Crystalline Solids. 299-302 (2002) 1147-1151.
- [5] M. Born and E. Wolf, *Principles of Optics*. 6th ed. Pergamon Press, 1980.

- [6] F.C. Marques, J. Urdanivia, and I. Chambouleyron, Solar Energy Materials and Solar Cells 52, (1998) 285-292.
- [7] M.R. Hantehzadeh, M. Ghoranneviss, A. H. Sari, F. Sahlani, A. Shokuhi and M. Shariati, Thin Solid Films 515 (2006) pp. 547-550.
- [8] F.C. Marques, Sprayed SnO₂ Antireflective Coating on Textured Silicon Surface for Solar Cell Applications, IEEE Transaction on Electron Devices 45 (7) 1619 (1998).
- [9] E. G. Birgin, I. Chambouleyron, and J. M. Martínez, Journal of Computational Physics 151 (1999) pp. 862-880.