O F

M. LIPIŃSKI*, R. MROCZYŃSKI**

OPTIMISATION OF MULTILAYERS ANTIREFLECTION COATING FOR SOLAR CELLS

OPTYMALIZACJA WIELOWARSTWOWYCH POKRYĆ ANTYODBICIOWYCH DLA OGNIW SŁONECZNYCH

In the work the optimization of SiO₂-SiN_x and SiO₂-SiN_{x1}-SiN_{x2} multilayer antireflection coatings deposited by RF-PECVD is presented. The computer simulation was carried out for planar and textured Si surfaces as well. It was shown that double layer SiO₂-SiN_x can improve the short circuit current J_{sc} about 1.8% for planar surfaces. The improvement for textured surfaces is equal about 0.8%. The predictions have been experimentally verified with multi-crystalline silicon solar cells electrical parameters. The highest short circuit current (30.17 mA/cm²) and conversion efficiency (13.84%) were obtained for solar cell with double layer AR coating. For triple AR coating the open circuit voltage was the highest (600 mV) which can be explained by better surface passivation. However, the short circuit current (29.79 mA/cm²) was lower in comparison with double AR coating due to higher absorption of this layer.

Keywords: antireflection coating, solar cells, silicon nitride, multilayer ARC

Przedstawiono wyniki optymalizacji podwójnej SiO₂-SiN_x i potrójnej SiO₂-SiN_{x1}-SiN_{x2} warstwy anty-refleksyjnej osadzanej metodą RF PECVD. Komputerowe symulacje wykonano zarówno na planarnych jak i teksturowanych powierzchniach płytek krzemowych. Pokazano, że warstwy SiO₂-SiN_x mogą zwiększyć prąd zwarciowy o 1.8% dla płaskiej powierzchni krzemu. Dla teksturowanej powierzchni krzemu wzrost przewidywany wzrost prądu zwarciowego wynosi 0.8%. Wyniki symulacji zostały zweryfikowane z elektrycznymi parametrami krzemowych ogniw słonecznych wykonanych z krzemu multi-krystalicznego. Najwyższe wartości prądu zwarciowego (30.17 mA/cm²) i sprawności konwersji (13.84%) uzyskano dla podwójnej warstwy AR. Dla potrójnej warstwy AR uzyskano najwyższą wartość napięcia obwodu otwartego V_{oc} (600 mV). Jest to efekt poprawy pasywacji powierzchni przez tą warstwę. Jednakże, prąd zwarciowy (29.79 mA/cm²) był niższy w porównaniu z ogniwem z warstwą podwójną w wyniku wyższej absorpcji tej warstwy.

1. Introduction

The bare non-textured surface of silicon reflects above 35% of the incident power of sunlight. In order to reduce the optical loses due to surface reflection the surface is textured and covered by an antireflection (AR) coating. The commercial solar cells usually have only one single layer AR (SLAR) coating which allows to reduce the average reflection loss to about 10%. The single layer AR coating allows to reach a very low reflectance at one certain wavelength due to the destructive interference of waves reflected at the top and bottom of the coating. The use of multilayer AR coating can reduce reflection over a broader band of wavelength with two or more minimum reflection depending of how many layers content the AR coating and their refraction indexes and thicknesses [1, 2]. Presently the SiN_x:H antireflection coatings deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) are used in the most solar cells. The SiN_x:H layer is very attractive antireflection coating due to the high optical parameters flexibility. The refractive index can be changed in a wide range (from 1.9-3.0 at 600 nm) by gas composition (SiH₄:NH₃) adjustment [3]. The great interest in SiN_x:H AR coatings is mainly connected with the two important properties for silicon solar cells, especially made on polycrystalline Si: they reduce the surface recombination velocity by passivating the surface in low temperature (instead of thermally grown in high temperature SiO₂) and can be used for bulk crystallographic defects passivation by the contained hydrogen. It was shown that surface passivation is more effective by high index n [4]. In the work

^{*} INSTITUTE OF METALLURGY AND MATERIALS SCIENCE OF POLISH ACADEMY OF SCIENCES, 30-059 KRAKÓW, 25 REYMONTA STR., POLAND

^{**} INSTITUTE OF MICROELECTRONIC AND OPTOELECTRONIC, WARSAW UNIVERSITY OF TECHNOLOGY, 00-662 WARSZAWA, 75 KOSZYKOWA STR., POLAND

[3] shown that optimal optical properties of graded index SiO_xN_y layers for solar cells can be obtained for an abrupt change of the material from SiO_2 to SiN_x , e.g. this layers can be reduced to double layer AR coating SiO_2-SiN_x with SiN_x having *n* about 2.2. This result is an effect of high absorption of SiN_x layer. Therefore, it seems that the double layer SiO_2-SiN_x has the best optical properties. However, regarding the effect of passivation it is interesting to consider the triple layer AR coatings $SiO_2-SiN_{x1}-SiN_{x2}$ where SiN_{x2} have the relatively high index and sufficient thickness [3]. Therefore, in the work the results of optimization of double and triple layer AR coatings are presented and first results of application this results into multi-crystalline silicon solar cells.

2. Experiment

Deposition of layers. The oxynitride films SiO_xN_y were deposited on polished single crystal of silicon (Cz-Si) wafers by an Oxford Plasma Technology PLAS-MALAB 80+ system described elsewhere [5]. The Plasma Enhanced Vapour Deposition (PECVD) process runs in parallel plate reactor in a RF-plasma (13.56 MHz). The temperature of the deposition processes was 350°C. The stoichiometry of the layers were adjusted by a different gas flow ratio SiH₄:NH₃: N₂O.

Optical constant. The optical parameters n and k in a function of wavelength were found from spectroscopic ellipsometry (ellipsometer VASE) measurements carried out for wavelength in the 270-1000 nm range. Figure 1 shows the obtained results of optical parameters: refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ of the layers.



Fig. 1. Refractive index *n* and extinction coefficient *k* of SiO_xN_y layers vs. wavelength λ

Simulation and optimization of AR coatings. The optical parameters n and k presented in Fig. 1 were used to design the multilayer antireflection coatings for silicon

solar cells with planar and textured surfaces. The double layers (DLAR) SiO₂-SiN_{x2} and triple layers (TLAR) SiO₂-SiN_{x2}-SiN_{x1} coatings were optimized for silicon solar cells with different internal quantum efficiency. The reflectance $R(\lambda)$ and absorption $A(\lambda)$ in function of the thickness of each sub-layer were simulated using SCOUT program [6] for planar and SUNRAY program for textured surfaces [7] and the density of short circuit current J_{sc} for each simulated multilayer AR coating was calculated according to eq.1:

$$J_{sc} = q \int_{300}^{1200} [(1 - R(\lambda) - A(\lambda)]Fph(\lambda)IQE(\lambda)d\lambda =$$

= $J_{sc\max} - J_{ref} - J_{ab},$ (1)

where $F_{ph}(\lambda)$ is the incident photon flux of AM1.5G solar spectrum, $R(\lambda)$ – reflectance, $A(\lambda)$ – absorption of ARC layer, $IQE(\lambda)$ – internal quantum efficiency, J_{scmax} – maximal current for black non-reflective surface ($J_{scmax} \approx 35.5 \text{ mA/cm}^2$ for IQE(2), 41.0 mA/cm² for IQE(1) from Fig. 2 and 45.1 mA/cm² for an "ideal" IQE = 1). The J_{sc} of planar cells was calculated for two internal quantum efficiency $IQE(\lambda)$ presented in Fig. 2 for solar cell with efficiency 16.6% (IQE(1)) and 24% (IQE(2)) and textured cells for IQE = 1. Additionally the current loses due to the reflection J_{ref} and absorption J_{ab} were calculated [3]. The influence of n index on the surface passivation effect by SiN_x was not considered in this simulation.



Fig. 2. Simulated internal quantum efficiency IQE of two solar cells (16.6% efficiency with IQE(2) and 24% with IQE(1), simulation by PC-1D program [8]) and incident photon flux F_{ph} of AM1.5 solar spectrum

Reflectance measurements. In order to experimentally verify the simulation results, the Cz-Si wafers were coated with optimized multilayer AR coatings. The total reflectivity of samples was measured using a Perkin-Elmer Lambda 19 spectrophotometer equipped with an integrating sphere. Silicon solar cells fabrication. The substrates used for solar cells fabrication were 'as-cut', boron doped p-type, 6 Ω ·cm multi-crystalline Si wafers "SOLSIX[®]". The thickness of the wafers was 220 µm and the area was 10×10 cm². The manufacturing sequence for the cell fabrication can be presented in the following points:

- 1. Saw damage removing by KOH etching
- 2. Emitter formation by phosphorus diffusion
- 3. Edge junction isolation
- 4. PECVD ARC deposition
- 5. Screen-printing front and back contacts
- 6. Co-firing front and back metal contacts

The metallization of solar cells was made by screen-printing process which is commonly used in industrial production. A silver paste PV145 was used for the front contact. The coverage of the surface cell by grid contact was 7%. The back contact covering the full rear surface was deposited with pure Al paste. Two collection back bus bar contacts were printed with a silver paste containing 3% (w. g.) aluminum paste. After screen-printing, the pastes were dried by heating at 200°C and subsequently co-fired in an infrared (IR) belt furnace (LA-310).

3. Results

Results of optimization. The results of optimization are presented in Table 1 for planar Si surface and in Table 2 for textured Si surface. It is seen that the highest calculated value of J_{sc} are for double layer AR coatings. The increase of J_{sc} is about 1.8% for planar surfaces and about 0.8% for textured surfaces relative to single layer SiN_x . In the case of triple layer AR coating the increase is about 1.4 for planar surface and there is no gain for textured surface relative to single layer. It is seen that, however, for triple layer AR coating on planar surface the value of J_{ref} is the smallest but the J_{ab} is considerably high due to absorption and dominates the value of J_{sc} . For triple layer AR coating the thickness of the first layer on Si substrate (SiN_{x1}) was assumed equal to 10 nm. Such value was chosen because thicker layer causes significant increase of absorption loss and in the other hand for thinner layer the surface passivation would be reduced [3]. The thicknesses of others layers $(SiN_{x1} and SiO_2)$ were optimized in order to obtain the maximum of J_{sc} .

The parameters of layers presented in Table 1 were used for deposition of multilayer AR coatings on polished Si wafers by RF PECVD. Figure 3 presents the results of reflectance measurements. It is seen that triple layer AR coating has smallest reflectance. The calculated J_{ref} for all the curves are nearly the same as presented in Table 1 for planar surfaces.

| TABLE | 1 |
|-------|---|

Results of the optimization of single, double and triple layer AR coatings. Reflection loss J_{ref} , absorption loss J_{ab} and short circuit current J_{sc} calculated for IQE(2). Additionally short circuit current J_{sc} for IQE(1) is shown. The thicknesses of layers are marked by d1, d2, d3

| f****** | | | | | | | |
|---------|------------|--------------|--------------|-----------------------|-----------------|-----------------|-----------------|
| AR | <i>d</i> 1 | <i>d</i> 2 | d3 | T. | T | J _{sc} | J _{sc} |
| coating | (SiO_2) | (SiN_{s1}) | (SiN_{x2}) | J _{ref} | J _{ab} | (IQE(2)) | (IQE(1)) |
| | [nm] | | | [mA/cm ²] | | | |
| SLAR | 0 | 76 | 0 | 2.85 | 0.46 | 32.16 | 36.75 |
| DLAR | 40 | 57 | 0 | 2.45 | 0.30 | 32.74 | 37.43 |
| TLAR | 42 | 44 | 10 | 2.33 | 0.57 | 32.57 | 37.30 |

TABLE 2

Results of the optimization of multilayer AR coatings on textured Si surface (by Sunrays program [7] for IQE = 1)

| AR coating | d1 (SiO ₂) | $\frac{d2}{(SiN_{x1})}$ | d3 (SiN _{x2}) | J _{ref} | J _{sc} |
|---------------|---------------------------|-------------------------|----------------------------|-----------------------|-----------------|
| | [nm] | | | [mA/cm ²] | |
| SLAR | 0 | 74 | 0 | 1.0 | 39.40 |
| DLAR | 44 | 57 | 0 | 0.7 | 39.70 |
| TLAR | 40 | 50 | 10 | 0.7 | 39.40 |



Fig. 3. Reflectance of multi-layers AR coatings deposited on polished silicon surfaces (Cz-Si) by RF PECVD

Solar cell results. Table 3 shows the electrical parameters of solar cells measured under standard AM1.5 (100 mW/cm²) radiation at 24°C. It is seen that short circuit current of mc-Si solar cell with DLAR coating SiO_2/SiN_{x1} is improved about 0.3% in comparison with cell with single layer AR coating SiN_x . The efficiency increases about 1.8% due to improvement of the open circuit voltage V_{oc} and fill factor *FF*. For the TLAR coating $SiO_2/SiN_{x1}/SiN_{x2}$ the short circuit current J_{sc} is smaller than for cell with single AR coating but the efficiency is higher due to improvement of V_{oc} . This highest value of V_{oc} can be connected with better surface passivation by this layer.

TABLE 3

The electrical parameters of the multi-crystalline Si solar cells: short circuit current J_{sc} , open circuit voltage V_{oc} , fill factor FFand efficiency E_{ff} measured under standard AM 1.5 radiation (100 mW/cm²) at 24°C

| AR coating | J _{sc} [mA/cm ²] | V _{oc} [mV] | FF [%] | $\begin{bmatrix} E_{ff} \\ [\%] \end{bmatrix}$ |
|---------------|--|-------------------------|-----------|--|
| SLAR | 29.86 | 596 | 74.6 | 13.38 |
| DLAR | 30.17 | 598 | 76.8 | 13.84 |
| TLAR | 29.79 | 600 | 75.6 | 13.47 |

4. Conclusions

It was shown that double layer SiO_2 -SiN_x can improve the short circuit current J_{sc} about 1.8% for planar surfaces. The improvement for textured surfaces is even smaller and is equal about 0.8%. The value of J_{sc} of the experimental solar cells made on mc-Si wafers with DLAR coating increases only 0.3% in comparison with single layer AR coating. This finding can be explained by the fact that simulation was made for planar polished surfaces and for theoretical internal quantum efficiencies which could differ from IQE of our solar cells. In the case of multi-crystalline material the surface etched in KOH is not homogenous and the lifetime of the minority may not be identical. It was shown that V_{oc} for the triple layer AR coating was improved. This can be explained by improvement of surface passivation by thin layer of SiN_{x2} with refractive index about 2.2. The simulation for textured surfaces shows that the improvement of short circuit current J_{sc} by double layer AR coating is smaller than for planar surfaces. This is caused by the fact that single layer AR coating deposited on textured surface has a very small reflectance and further reduction of reflectance by application of double or triple layer AR coatings is relatively very small.

Acknowledgements

This was supported by Polish Ministry of Science and Higher Education in the frame of the Project PBZ /100/T08/2003. The author

Received: 3 December 2007.

would like to thank Prof. R.B. Beck from Institute of Microelectronics and Optoelectronics, Warsaw University of Technology, for the SiO_xN_y layers deposition, H. Czternastek from AGH in Cracow for reflectance measurements and W. Rzodkiewicz from ITE in Warsaw for ellipsometric measurements.

REFERENCES

- D. N. Wright, E. S. Marstein, A. Holt, Double Layer Anti-reflective Coatings for Silicon Solar Cells, Proceedings of the 31st IEEE Photovoltaic Specialists Conference, Orlando, 1237-1240 (2005).
- [2] B. Kumar, T. B. Pandian, E. Sreekiran, S. Narayanan, Benefit of dual layer silicon nitride anti-reflection coating, Proceedings of the 31st IEEE Photovoltaic Specialists Conference, Orlando, 1205-1208 (2005).
- [3] M. Lipiński, A. Kamiński, J.-F. Lelievre, M. Lemiti, E. Fourmond, P. Zięba, Investigation of graded index SiOxNy antireflection coating for silicon solar cell manufacturing, phys. stat. sol. (c), 4, 4, 1566-1569 (2007).
- [4] T. L a u i n g e r, A. G. A b e r l e, R. H e z e l, Comparison of direct and remote PECVD silicon nitride films for low temperature surface passivation of p type crystalline silicon, Proceedings of the 14th European Photovoltaic Solar Energy Conference, Barcelona, Spain, 853-856 (1997).
- [5] R. Mroczyński, R. B. Beck, The influence of dilution of the reactive gases in argon on electro-physical properties of ultra-thin silicon oxynitride layers formed by PECVD, Vacuum 81, 5, 695-699 (2007).
- [6] W. Theiss, Hard- and Software for Optical Spectroscopy, version 2.3, www.mtheiss.com
- [7] SUNRAYS program 1.3 and user manual is distributed by Garching Innovation GmbH, c/o M. Pasecky, Königinstr. 19, D-80539 München, Germany, Fax +49-89-21081593.
- [8] P. A. Basore, D. A. Clugsto, PC1-D version 4 for windows: from analysis to design, Proceedings of the 25th IEEE Photovoltaic Specialists Conference, Washington, 377-381(1996).