

# New designs for graded refractive index antireflection coatings

A. Mahdjoub<sup>a,\*</sup>, L. Zighed<sup>b</sup>

<sup>a</sup>Département de physique, Centre universitaire L.Benmehdi, BP358 OEB 04000 O.E.Bouaghi, Algeria

<sup>b</sup>Département d'Electronique, Université de Skikda, Algeria

Received 25 March 2004; accepted in revised form 11 November 2004

Available online 10 December 2004

## Abstract

The incessant progress in thin layers technology, especially the graded index inhomogeneous dielectrics, allows the realization of antireflection coatings (ARCs). Graded refractive index silicon oxynitrides are deposited by electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) controlled in situ by monochromatic ellipsometry. While avoiding the complexity of the classical multilayer ARCs, graded coatings permit to obtain the same performances, or furthermore to improve solar cells efficiency. A theoretical model, validated by confrontation to ellipsometric spectra, and reflectance measurements were used to optimize different suggested profiles. Calculation predicts an enhancement of photogenerated current exceeding 45% and a weighted reflectance (between 300 and 1100 nm) around 5.6%. On texturized surfaces, these ARCs should enhance short-circuit current by 52.79%.

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PACS: 42.79; 84.60-Jt; 78.40-q; 81.15-z; 81.15-Gh

Keywords: ARCs; Oxynitrides; Ellipsometry; Graded refractive index

## 1. Introduction

Materials used for the manufacture of solar cells (Si, GaAs, InP, CdTe, etc.) present high refractive indices; thus, more than 35% of incident sunlight is lost by reflection without antireflection coating (ARC) [1]. The quality of ARC is therefore an essential parameter to obtain high-efficiency solar cells [2–4]. The simplest way to realize ARC, usually used in photovoltaic industry, consists in depositing a quarter wavelength dielectric layer with high refractive index (TiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, SiO, etc.). For example, for silicon solar cells, Si<sub>3</sub>N<sub>4</sub> ARC centered on the maximum of AM0 solar spectrum, reduces reflections to 12% on average in the 400–1100 nm wavelength range. Short-circuit current is increased by 45% [1]. Multilayer systems combined with surface texturization can reduce reflection losses to few percents over all the useful range of solar spectrum [2,5–7]. However, the more technically complicated is the production, the higher is the cost.

Another practical manner to reduce reflection consists in depositing an inhomogeneous dielectric with a gradual decrease of refractive index from substrate to the ambient. It is, therefore, necessary to optimize the refractive index profile to get minimum reflectance. Neuman [7] reported that antireflection performance of graded index coatings is less sensitive to thickness changes compared to classical ARCs.

The steady progress in thin layers technology, especially inhomogeneous dielectrics with variable refractive index, arouses researchers' interest who suggested new deposition techniques [8–10], modelization and characterization methods [11–13]. Therefore, our studies were guided toward graded refractive index ARC for solar cells applications. The most important advantage of the manufacture of these layers is the possibility to make a full system having a complex profile at one deposition stage without interruption of plasma process; hence, in so doing, the problem of interfaces will be avoided. Among the studied inhomogeneous dielectrics, oxynitrides seem particularly interesting [14,15]. Since they are intermediate compounds between silica and nitrides, oxynitrides encom-

\* Corresponding author. Tel.: +213 32 42 39 70; fax: +213 32 42 10 36.  
E-mail address: [abdelmah@yahoo.com](mailto:abdelmah@yahoo.com) (A. Mahdjoub).

pass mechanical and dielectrical qualities of silica, and present the advantage of serving as a diffusion barrier to impurities, like nitrides. Transparent in visible and near infrared, their refractive indices can vary between those of  $\text{Si}_3\text{N}_4$  (2.015 at 633 nm) and  $\text{SiO}_2$  (1.457 at 633 nm) [16]. Thus, oxynitrides allow the realization of good-quality graded index films.

There are several deposition methods of graded index layers; we chose microwave electron cyclotron resonance plasma-enhanced chemical vapor deposition (ECR-PECVD) because high-quality materials can be obtained at low temperatures [17,18].

The present work aims at designing silicon oxynitrides graded index antireflective coatings for solar application. A theoretical model is used to study the optical behavior of these ARCs at normal and oblique incidence. After validation of the model by confrontation with ellipsometric spectra and reflectance measurements, the optimum conditions for graded index ARC realization will be brought out using different possible profiles.

## 2. Theoretical model

The reflectance of graded index dielectric systems is a classical problem dealt with according to different approaches [11,12]. The stratified medium theory with its matrix representation presents the advantage of simple formalism and great flexibility in use [19,20]. The inhomogeneous dielectric is subdivided into  $N$  homogeneous strata of equal thickness  $d$ , with index  $\tilde{N}_j$  variable versus depth. The Bruggeman effective medium approximation (BEMA) [19–21] permits the determination of  $\tilde{N}_j$  from volume fractions  $f_A$ ,  $f_B$  and already known refractive indices  $\tilde{N}_A$  and  $\tilde{N}_B$  of silica and silicon nitride, respectively. For two-component system, BEMA is written:

$$f_A \frac{\tilde{N}_A^2 - \tilde{N}_j^2}{\tilde{N}_A^2 + 2\tilde{N}_j^2} + f_B \frac{\tilde{N}_B^2 - \tilde{N}_j^2}{\tilde{N}_B^2 + 2\tilde{N}_j^2} = 0 \quad \text{with } f_A + f_B = 1 \quad (1)$$

Although oxynitrides are not physical mixtures of silica and silicon nitride, the BEMA is an approximation which gives satisfactory results in visible and near-infrared range [11].

For silicon bulk, silica and silicon nitride, we used refractive indices published by Palik [16].

To obtain graded index layer, we have to change volume fractions  $f_A$  and  $f_B$  with a variation law versus depth according to the desired profile.

Each stratum is represented by a complex characteristic matrix  $\mathbf{M}_j$ . Matrices  $\mathbf{M}_0$  and  $\mathbf{M}_s$  correspond to ambient and substrate semi-infinite media respectively [19].

We can then write the simplified relation:

$$\begin{bmatrix} a \\ b \end{bmatrix} = \mathbf{M}_0 \left( \prod_{j=1}^N \mathbf{M}_j \right) \mathbf{M}_s \quad (2)$$

In a more explicit way:

$$\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} p_0^{-1} \\ p_0^1 \end{bmatrix} \prod_{j=1}^N \begin{bmatrix} \cos \delta_j & p_j^{-1} \sin \delta_j \\ ip_j \sin \delta_j & \cos \delta_j \end{bmatrix} \begin{bmatrix} 1 \\ p_s \end{bmatrix} \quad (3)$$

where  $\delta_j$  is the phase shift due to the  $j$ th stratum

$$\delta_j = \frac{2\pi}{\lambda} \tilde{N}_j d_j \cos \theta_j \quad (4)$$

and  $\theta_j$  is determined from incident angle  $\theta_0$  using Snell–Descartes law:

$$\tilde{N}_j \sin \theta_j = \tilde{N}_0 \sin \theta_0 \quad (5)$$

For transverse electric (TE) polarization  $p_j = \tilde{N}_j \cos \theta_j$  and for transverse magnetic (TM) polarization,  $p_j = \tilde{N}_j / \cos \theta_j$ .

Fresnel coefficients are calculated for both polarizations and for each wavelength from the relations:

$$R_{\text{TE}} = \left( \frac{a}{b} \right)_{\text{TE}} \quad \text{and} \quad R_{\text{TM}} = \left( \frac{a}{b} \right)_{\text{TM}} \quad (6)$$

Since sunlight is unpolarized, the total reflectance is half from TE and half from TM waves:

$$R = 0.5(R_{\text{TE}} R_{\text{TE}}^* + R_{\text{TM}} R_{\text{TM}}^*) \quad (7)$$

Fresnel reflection coefficients express changes in amplitude and phase of electric vector for TE and TM polarization. An ellipsometer measures the ratio of TM-state to TE-state Fresnel coefficients which are expressed according to the ellipsometric angles  $\Psi$  and  $\Delta$  by the relation:

$$\rho = \frac{R_{\text{TM}}}{R_{\text{TE}}} = \text{tg}(\psi) \exp(i\Delta) \quad (8)$$

## 3. Criteria for antireflection coatings design

Although minimizing the reflectivity is highly desirable, it is not the best criterion to optimize an ARC. The spectral aspect of incident sunlight and the internal spectral response have to be taken into account. The weighted average reflectance  $R_W$  between  $\lambda_1$  and  $\lambda_2$  is defined as [22]:

$$R_W = \frac{\int_{\lambda_1}^{\lambda_2} R(\lambda) \Phi(\lambda) S(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} \Phi(\lambda) S(\lambda) d\lambda} \quad (9)$$

where  $\phi(\lambda)$  is the spectral irradiance of sunlight, and  $S(\lambda)$  the internal spectral sensitivity of the solar cell.

Zhao and Green [3] consider that photo-generated current is the best criterion for ARC design. Indeed, the direct consequence of antireflective coatings deposition is the increase of photo-generated current [2,3,20]. The

density of the short-circuit current, photo generated in the range  $[\lambda_1, \lambda_2]$ , can be calculated by the relation [22]:

$$J_{SC} = \int_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] \Phi(\lambda) S(\lambda) d\lambda \quad (10)$$

$\phi(\lambda)$  was calculated from AM1.5 solar spectrum [22], and  $S(\lambda)$  values used in this work were those of ordinary c-Si solar cell, published by Orgeret [22]. The integration covers the sensitive range of silicon cell between 300 and 1100 nm.

$R_W$  has always its minimum when  $J_{SC}$  is optimized. Indeed, we can also express the weighted reflectance by:

$$R_W = 1 - \frac{J_{SC}}{J_{SC}(R=0)} \quad (11)$$

where  $J_{SC}(R=0)$  corresponds to  $J_{SC}$  in ideal case (without reflection losses).

The improvement in  $J_{SC}$  due to the use of ARC will be therefore:

$$\frac{\Delta J_{SC}}{J_{SC}} = \frac{J_{SC}(\text{with ARC}) - J_{SC}(\text{without ARC})}{J_{SC}(\text{without ARC})} \quad (12)$$

In literature, we assign the best improvement in  $J_{SC}$  (50–60%) principally to the reduction in reflection losses, but also partially to the surface passivation which reduces the surface recombination rate [23–25]. In our case, only the losses by reflection are considered.

#### 4. Experimental details

The oxynitrides films were deposited by ECR-PECVD with the same conditions as silica or silicon nitride films. We used  $\text{SiH}_4$  as silicon precursor and a plasma constituted from nitrogen and oxygen. The simplest method to obtain graded index films is to modify the  $\text{SiO}_x\text{N}_y$  composition by varying the gas ratios in the plasma during film growth. As oxygen is much reactive than nitrogen, a small variation of  $\text{O}_2$  flow rate results in sizeable index changes. For this reason, and to simplify the procedure of deposition, all parameters were maintained constant except the oxygen flow rate which increases from 0.5 to 2 sccm.  $\text{SiH}_4$  and  $\text{N}_2$  flow rates were set at 4 and 20 sccm, respectively. Total pressure in the deposition chamber, measured by a baratron gauge, was typically 1.5 mTorr. Silicon substrate (100) was heated to 200 °C, and the distance to the ECR source was 15 cm. In these conditions, typical variation of refractive indices at 633 nm from 2 to 1.45 can be obtained. We can then elaborate graded index oxynitrides layers with different profiles using regulation of oxygen flow rate during deposition (automatic control piloted by computer). The classical ellipsometric method for in situ control [26] consist to

following the trajectory of  $\Psi$  and  $\Delta$  angles during the deposition at a given wavelength (633 nm in our case). The  $\Delta$  versus  $\Psi$  curve is plotted in a cartesian coordinates and compared to theoretical abacus obtained for different fixed refractive index. The sample used in this work is constituted from silicon oxynitrides layer with near-linear profile, deposited on monocrystalline silicon substrate. In situ ellipsometric investigations permit the approximate evaluation the thickness (around 270 nm) and the variation of refractive index in the range (2–1.5), between the beginning and the end of deposition. The spectroscopic ellipsometry allows more accurate determination of thickness and refractive index.

For evaluating the performance of graded ARCs, reflectance measurements have been taken from the sample after deposition using a Cary-5G ultraviolet-visible-infrared spectrophotometer.

#### 5. Theoretical model validation

To simulate near-linear profile, we use for volume fraction of silica in the oxynitrides film, a function like:

$$f_A = f_0 - (f_0 - f_F) \left( \frac{x}{E} \right)^\alpha \quad (13)$$

where  $f_0$  and  $f_F$  are silica volume fractions at the ARC surface and interface ARC/Si, respectively. The variable  $x$  represents the depth in ARC, and  $E$  the thickness of ARC. The form parameter  $\alpha$  describes a possible deviation from linearity in index profile.

The profiles of refractive index reported in Fig. 1 were calculated from BEMA (Eq. (1)) at 633 nm for  $f_0=1$  and  $f_F=0$ .

In order to calculate  $\Psi$ ,  $\Delta$  and  $R$ , the graded index layer is divided into homogenous strata of equal thickness. The number of strata used depends on profile complexity; for linear profile, 20 strata are sufficient.

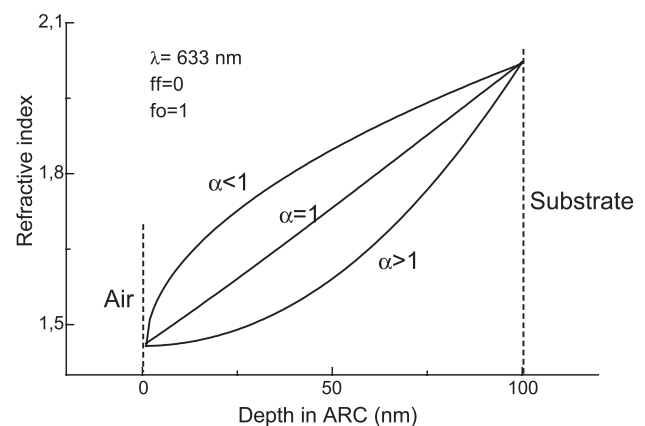


Fig. 1. ARCs with graded index profiles.

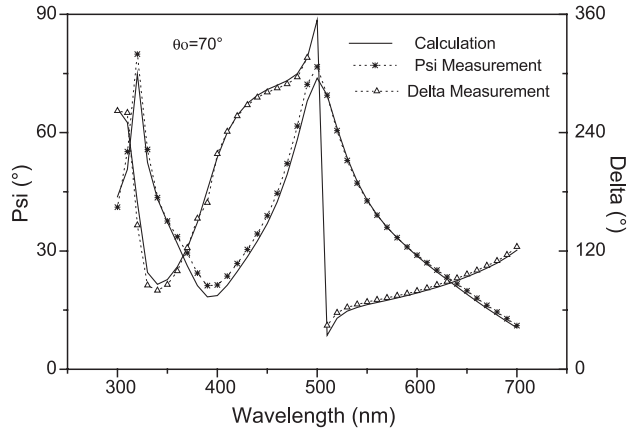


Fig. 2. Theoretical and experimental ellipsometric spectra of linear graded ARC.

The regression analysis method consists of varying the model parameters in order to minimize error function expressed by:

$$\chi = \frac{1}{2M} \sum^M \left[ \lg(\psi_{\text{exp}}) - \lg(\psi_{\text{Th}}) \right]^2 + [\cos(\Delta_{\text{exp}}) - \cos(\Delta_{\text{Th}})]^2 \quad (14)$$

where  $M$  represents the number of measurements ( $\psi_{\text{exp}}$ ,  $\Delta_{\text{exp}}$ ) by spectrum, taken at  $70^\circ$  of incidence, between 300 and 700 nm.  $\psi_{\text{Th}}$ ,  $\Delta_{\text{Th}}$  are calculated values of ellipsometric angles.

In our case, the results obtained by minimization are plausible. The minimum of error function obtained is  $\chi_{\min} = 4.5 \times 10^{-3}$ . This result is comparable with those mentioned in the literature [11,16]. The oxynitride film deposited with a thickness of 275 nm presents a practically linear gradient ( $\alpha=0.95$ ). The volume fraction of silica varies from  $f_0=97\%$  to  $f_F=31\%$  corresponding to variation of refractive index between 1.85 and 1.47 at 633 nm. A good agreement between theoretical and experimental ellipsometric spectra is shown in Fig. 2. These results confirm with more precision the in situ ellipsometric investigations. The

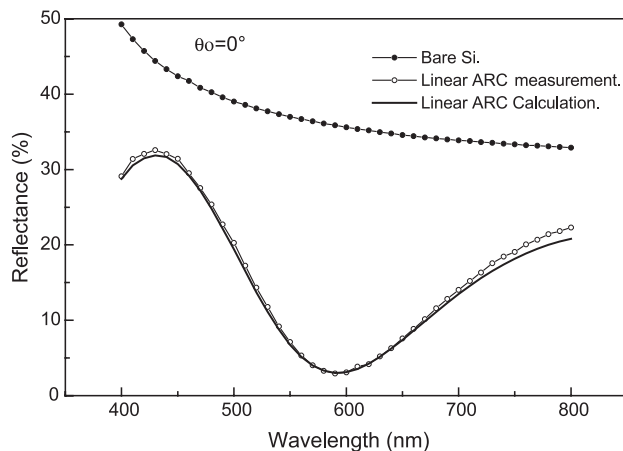


Fig. 3. Reflectance of linear graded ARC compared to that of bare silicon.

parameters obtained by minimization allow the calculation at normal incidence of the reflectance spectrum between 400 and 800 nm. The theoretical curve corresponds well to experimental measurements (Fig. 3). These results permit to validate the model used to simulate the optical behavior of such oxynitrides layers.

We can also notice that reflection losses are considerably reduced (18% of average reflection with graded index layer versus 35% for bar silicon). The optimization of parameters (thickness and refractive index profile) of such dielectric films allows the realization of ARCs with high performances.

## 6. Optimization results

Different profiles can be suggested and defined as previously by the function describing the variation of silica volume fraction. We have studied the two following models:

- To replace a classical homogenous monolayer ARC, we propose a gradient described by Eq. (13) mentioned in the preceding paragraph. So as highlight influence of index profile on the ARC performances, we have taken three values for  $\alpha$ :  $\alpha=1$ ,  $\alpha=0.5$  and  $\alpha=2$  for linear, supralinear and sublinear profiles, respectively (see Fig. 1).
- To replace a classical double layer ARC, we used a new 'Fermi' profile, described by the following function:

$$f_A = f_F - (f_F - f_0)[1 + \exp((x - x_0)/\beta)]^{-1} \quad (15)$$

In this expression, the parameter  $\beta$  describes the form of the profile ( $\beta=5$  in Fig. 4). In the limit condition ( $\beta$  close to zero), we obtain the configuration of classical double layer ARC. Then, the inflection point  $x_0$  represents silicon oxide thickness.

For the two functions (Eqs. (13) and (16)), we used ideal limits conditions for  $\text{SiO}_2$  volume fraction:  $f_0=1$  and  $f_F=0$  corresponding to the largest refractive index gradient.

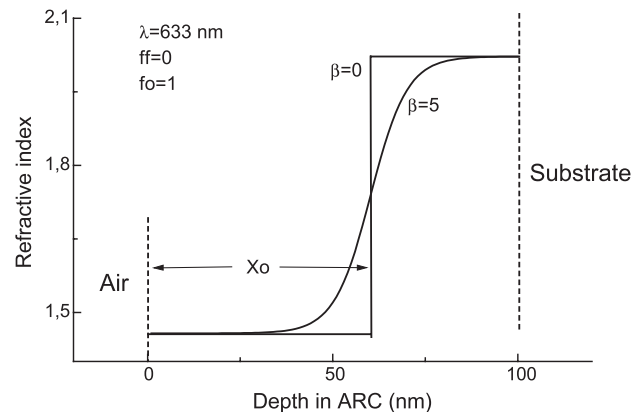


Fig. 4. ARC with 'Fermi' graded refractive index profile.

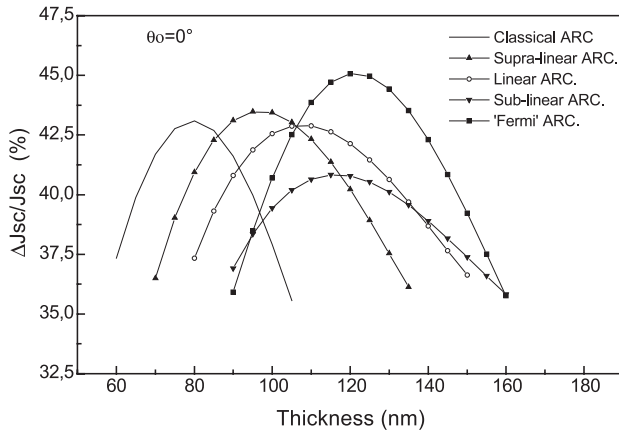


Fig. 5. Calculated improvement of short-circuit current. Graded ARCs compared to  $\text{Si}_3\text{N}_4$  classical coating.

The variation of improvement in  $J_{\text{SC}}$  versus total thickness of ARCs is shown in Fig. 5 for different profiles compared with  $\text{Si}_3\text{N}_4$  classical monolayer ARC. Linear and sublinear profiles do not seem appropriate. The supralinear profile should give good results: The calculation predicts 6.6% weighted average reflectance and 43.5% improvement in  $J_{\text{SC}}$ . The new 'Fermi' profile realizable in a single technological stage should improve significantly the performances of graded index ARCs. For optimal conditions  $\beta=5$ ,  $x_0=60$  nm and 120 nm thickness, 5.6% weighted average reflectance and 45.1% improvement in  $J_{\text{SC}}$  are expected (see also Fig. 6). These results are comparable with those obtained by Richards et al. [27] with classical double-layer ARCs.

The results presented in Table 1 are calculated for normal incidence. Associated with a prior texturization of the semiconductor surface, the graded ARCs should reduce the average reflection to less than few percents, and will tend to approximate the ideal case (without reflection losses). The improvement of the photocurrent should be:  $\Delta J_{\text{SC}}/J_{\text{SC}}=53.76\%$ .

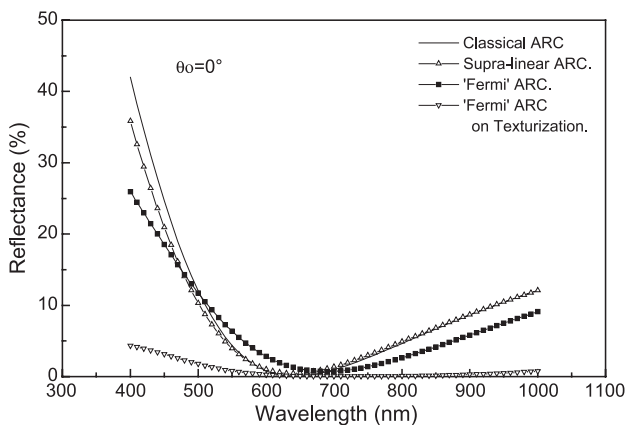


Fig. 6. Calculated reflectance of best graded ARCs compared to that of  $\text{Si}_3\text{N}_4$  classical coating.

Table 1  
Optimization results

ARCs	Optimal thickness (nm)	$\Delta J/J$ (%)	$R_W$ (%)
$\text{Si}_3\text{N}_4$ classical ARC	80	43.1	7.0
Supralinear ARC ( $\alpha=0.5$ )	95	43.5	6.6
Linear ARC ( $\alpha=1$ )	100	42.9	6.9
Sublinear ARC ( $\alpha=2$ )	115	40.8	8.3
'Fermi' ARC ( $\beta=5$ ; $x_0=60$ nm)	120	45.1	5.6

Nubile [20] proposes that the simplest approach to calculate the reflectivity of grooved surface is to use the approximate relation:

$$R_{\text{Tex}}(\lambda) = [R(\lambda, \theta_0 = \pi/4)]^2 \quad (16)$$

He considers that, on average, the light is reflected twice at  $45^\circ$ . While replacing the obtained values in the previous expressions of short-circuit current and weighted average reflectance, we obtained  $\Delta J_{\text{SC}}/J_{\text{SC}}=52.79\%$  and  $R_W=0.63\%$ . This calculation did not consider the effects of texturization on the surface recombination velocity. Damages caused by texturization can decrease the collection efficiency [28]. However, if one takes into account the passivation effect of oxynitrides, mentioned by many authors [23–25], the proposed system should improve considerably the performance of solar cells with easy technological process.

Perspectives for using other materials, like mixtures of silicon and titanium oxides [29], deposited by ECR-PECVD are in study, and other profiles can be suggested. The greater gradient, due to  $\text{TiO}_2$  high refractive index (2.3 at 500 nm), should improve even more the performances of such ARCs.

## 7. Conclusion

Silicon oxynitrides graded index antireflective coatings enhance solar cells' efficiency by reducing reflection losses and recombination rate in surface with adequate technological process. The suggested theoretical model simulates correctly the behavior of such optical system and permits to optimize the performances of silicon solar cells by determining the best conditions of realization of graded index ARCs. We can advantageously use passivating oxynitrides with graded index on texturized surface. Then, improvement in short-circuit current of 52.79% and 0.63% weighted average reflection between 300 and 1100 nm could practically be obtained. Perspectives of realization of the same type of ARCs with other materials are in the process of being studied.

## Acknowledgements

We would like to thank the research group of Professor J. Joseph of ECLyon, especially A.S. Callard and A. Gagnaire, for their assistance in accomplishing this work. We also



would like to thank R. Dubend and B. Devif for technical support.

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