ENGINEERING TRANSACTIONS • *Engng. Trans.* • **53**, 2, 185–196, 2005
Polish Academy of Sciences • Institute of Fundamental Technological Research
10.24423/engtrans.441.2005

NEW DESIGNS FOR GRADED REFRACTIVE INDEX ANTIREFLECTION COATINGS

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The constant progress in thin layers technology, especially the graded index inhomogeneous dielectrics, allows the realization of antireflection coatings (ARC) that are less sensitive to thickness and to the incidence angle. 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, the obtained AR coatings permit to obtain the same performances, or furthermore to improve the cells efficiency. Different suggested profiles are optimized by simulation, then they are realized and characterized by spectroscopic ellipsometry and reflectance measurement. The photogenerated current can be enhanced by 45%, and weighted reflectance (between 300 and 1100 nm) reduced to 5.6%. The passivating properties of oxinitrides recommend the use of these AR coatings on texturized surfaces. The weighted reflectance would decrease to less than 1% and short-circuit current will thus be enhanced by 52.79%.

Key words: AR coatings, oxinitrides, ellipsometry, graded refractive index.

1. INTRODUCTION

Materials used for the manufacture of solar cells (Si, GaAs, InP, CdTe…) present high refractive indices; thus more than 35% of the incident sunlight is lost by reflection without antireflection coating [1]. The quality of AR coating is therefore an essential parameter to obtain high-efficiency solar cells [2–4]. The simplest way to realize ARC, usually applied in photovoltaic industry, consists in deposing a quarter-wavelength dielectric layer with high refractive index (TiO_2, Si_3N_4, SiO…). For example for silicon solar cells, Si_3N_4 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 a heterogeneous dielectric with a gradual decrease of refractive index from substrate to the ambient. If this condition is satisfied, theoretically the reflection would be null. In practice we can only approach this ideal case because high-index materials are generally absorbent.

The steady progress in thin layers technology, especially heterogeneous dielectrics with variable refractive index attracts researchers interest who suggested new deposition techniques [8–10], modelling and characterization methods [11–13]. Therefore, our studies were guided toward graded refractive index antireflective coating (ARC) for solar cells applications. The most important advantage of manufacturing of these layers is the possibility to make a full system having a complex profile at one deposition stage without interruption of the plasma process; hence, in so doing, the problem of interfaces will be avoided. Among the studied inhomogeneous dielectrics, oxynitrides seem to be particularly interesting [14–15]. Since they are intermediate compounds between the silica and nitrides, oxinitrides encompass mechanical and dielectrical qualities of silica and present the advantage of serving as a diffusion barrier to such impurities like nitrides. Transparent in visible and near infrared, their refractive indices can vary between those of Si_3N_4 (2.04 at 500 nm) and SiO_2 (1.43 at 500 nm). Thus, oxynitrides allow the realization of good quality graded index films.

There are several deposition methods of graded index layers; we have chosen microwave electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR PECVD), because high quality materials can be obtained at low temperatures [16–17].

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 presented 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 [18–19]. The inhomogeneous dielectric is subdivided into N homogeneous strata of equal thickness d, indices $\tilde{N}_j$ with variable versus depth. The Bruggeman effective medium approximation BEMA [18–20] permits the determination of $\tilde{N}_j$ from volume fractions f_A, f_B and the already known refractive indices $\tilde{N}_A$ and $\tilde{N}_B$ of silica and silicon nitride respectively. For two components system BEMA is written:

$$f_A \frac{\tilde{N}_A^2 - \tilde{N}_j^2}{\tilde{N}_A^2 + 2\tilde{N}_j^2} + f_B \frac{\tilde{N}_B^2 - \tilde{N}_j^2}{\tilde{N}_B^2 + 2\tilde{N}_j^2} = 0 \quad \text{with} \quad f_A + f_B = 1. \tag{2.1}$$

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

For silicon bulk, silica and silicon nitride, we use refractive indices published by PALIK [21].

To obtain the 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 M_j. Matrices M_0 and M_s correspond to ambient and substrate semi-infinite media respectively [17].

We can then write the simplified relation:

$$\begin{bmatrix} a \\ b \end{bmatrix} = M_0 \cdot \left(\prod_{j=1}^{N} M_j \right) \cdot M_S. \tag{2.2}$$

In a more explicit way:

$$\begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} p_0 & -1 \\ p_0 & 1 \end{bmatrix} = \prod_{j=1}^{N} \begin{bmatrix} \cos\delta_j & p_j^{-1}\sin\delta_j \\ ip_j \sin\delta_j & \cos\delta_j \end{bmatrix} \begin{bmatrix} 1 \\ p_S \end{bmatrix} \tag{2.3}$$

where δ_j is the phase shift due to the j-th stratum

$$\delta_j = \frac{2\pi}{\lambda} \tilde{N}_j d_j \cos\theta_j \tag{2.4}$$

and θ_j is determined from the angle of incidence θ_0 using Snell–Descartes law:

$$\tilde{N} \sin\theta_j = \tilde{N}_0 \sin\theta_0. \tag{2.5}$$

For TE polarization $p_j = \tilde{N}_j \cos\theta_j$ and for TM polarization $p_j = \tilde{N}_j / \cos\theta_j$.

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

$$R_{\text{TE}} = \left(\frac{a}{b}\right)_{\text{TE}} \quad \text{and} \quad R_{\text{TM}} = \left(\frac{a}{b}\right)_{\text{TM}} \tag{2.6}$$

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

$$R = 0.5(R_{\text{TE}} \cdot R_{\text{TE}}* + R_{\text{TM}} \cdot R_{\text{TM}}*). \tag{2.7}$$

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

$$\rho = \frac{R_{\mathrm{TM}}}{R_{\mathrm{TE}}} = \mathrm{tg}(\psi) \cdot \exp(i\Delta). \tag{2.8}$$

3. CRITERIA FOR AR COATINGS DESIGN

Although minimizing the reflectivity is highly desirable, it is not the best criterion to optimize an AR coating. The spectral aspect of incident sunlight $\phi(\lambda)$ and the internal spectral sensitivity $S(\lambda)$ have to be taken into account. The weighted average reflectance R_W between λ_1 and λ_2 is defined as [22]:

$$R_W = \frac{\int\limits_{\lambda_1}^{\lambda_2} R(\lambda) \cdot \Phi(\lambda) \cdot S(\lambda)\, d\lambda}{\int\limits_{\lambda_1}^{\lambda_2} \Phi(\lambda) \cdot S(\lambda)\, d\lambda}. \tag{3.1}$$

ZHAO *et al.* [3] consider that photo-generated current is the best criterion for AR coating design. Indeed, the direct consequence of antireflective coatings deposition is the increase of photo generated current [2, 3, 19]. The density of the short-circuit current, photo-generated in the range $[\lambda_1, \lambda_2]$, can be calculated by the relation:

$$J_{SC} = \int\limits_{\lambda_1}^{\lambda_2} [1 - R(\lambda)] \cdot \Phi(\lambda) \cdot S(\lambda)\, d\lambda, \tag{3.2}$$

where $\phi(\lambda)$ is the incident solar flux, and $S(\lambda)$ the internal spectral sensitivity of the solar cell. $\phi(\lambda)$ was calculated from the AM1.5 solar spectrum, and $S(\lambda)$ values used in this work were 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:

$$R_W = 1 - \frac{J_{SC}}{J_{SC}(R=0)}, \tag{3.3}$$

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:

$$\Delta J_{SC} / J_{SC} \text{ (3.4)} \quad \frac{\Delta J_{SC}}{J_{SC}}=\frac{J_{SC}\,(\text{with ARC})-J_{SC}\,(\text{without ARC})}{J_{SC}\,(\text{without ARC})}. \tag{3.4}$$

In literature we assign the best improvement in J_{SC} (50 to 60%) principally to the reduction in reflection losses, but also partially to the surface passivation which reduces the surface recombination rate [23–24]. In our case only the losses by reflection are considered.

4. Experimental details and model validation

The oxynitrides films were deposited by ECR PECVD with the same conditions as the silica or silicon nitride films. We used SiH_4 as silicon precursor and a plasma consisting of nitrogen and oxygen. The simplest method to obtain graded index films is to modify the SiO_xN_y composition by varying the gas ratios in the plasma during film growth. As oxygen is much reactive than nitrogen, a small variation of 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 increase from 0.5 to 2 sccm. SiH_4 and N_2 flow rates were set at 4 sccm and 20 sccm, respectively. Total pressure in the deposition chamber, measured by a baratron gauge, was typically 1.5 mT. 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 prepare the graded index oxynitrides layers with different profiles using regulation of oxygen flow rate during deposition (automatic control piloted by computer). The sample used in this work is made from silicon oxynitrides layer with a nearly linear profile, deposited on monocristalline silicon substrate. *In-situ* ellipsometric measurements indicate a thickness around 270 nm and a variation of refractive index (at 633 nm) from 2 to 1.5 between the beginning and the end of deposition. Ellipsometric spectra and reflectance measurements have been taken from the sample after deposition (*ex-situ*).

To simulate near-linear profile of refractive indice (Fig. 1), we use for the volume fraction of silica in the oxynitrides film a function like :

$$f_A=f_0-(f_0-f_F)\left(\frac{x}{E}\right)\alpha, \tag{4.1}$$

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

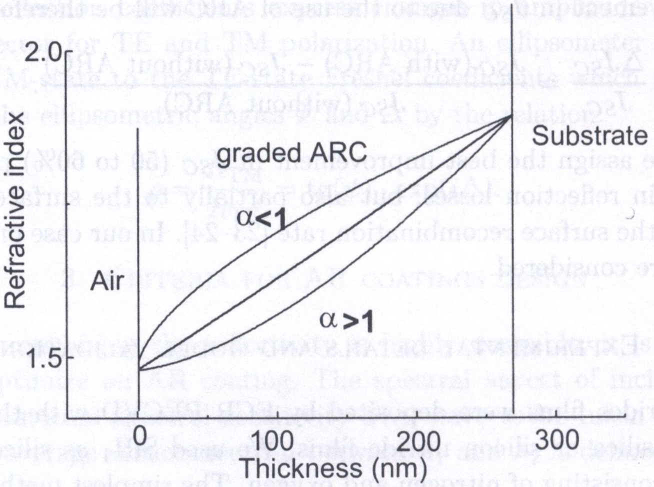

FIG. 1. AR coatings with graded index profile.

In order to calculate Ψ, Δ and R, the graded index layer is divided into homogenous strata of equal thickness. The indices of each stratum are obtained by BEMA using f_A defined by the preceding function. The number of strata used depends on profile complexity; for a linear profile 20 strata are sufficient.

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

$$\chi = \frac{1}{2M}\sum^{M}\left[\mathrm{tg}(\psi_{\mathrm{exp}}) - \mathrm{tg}(\psi_{Th})\right]^2 + \left[\cos(\Delta_{\mathrm{exp}}) - \cos(\Delta_{Th})\right]^2, \tag{4.2}$$

where M represents the number of measurements (ψ_{exp}, Δ_{exp}) by spectrum, taken at 70° angle of incidence, between 300 and 700 nm. ψ_{Th}, Δ_{Th} are the calculated values of ellipsometric angles.

In our case, the results obtained by minimization are plausible. The minimum of error function obtained is $\chi_{\min} = 4.5 \cdot 10^{-3}$. This result is comparable with those mentioned in the literature [11–16]. The oxynitride film deposited with a thickness of 275 nm presents a gradient practically linear ($\alpha = 0.95$) for a volume fraction of silica varying from $f_0 = 97\%$ to $f_f = 31\%$. 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 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 the experimental measurements (Fig. 3). These results permit to validate the model used to simulate the optical behavior of such oxynitrides layers. We can clearly notice that reflection losses are considerably reduced (18% of the average reflection with graded indice layer versus 35% for the bar silicon). The optimization of parameters of such dielectric films allows the realization of AR coatings with high efficiency.

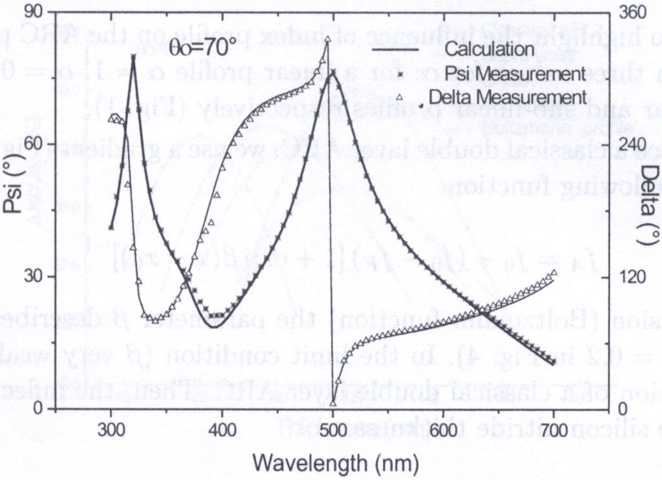

FIG. 2. Theoretical and experimental ellipsometric spectra of linear graded AR coating.

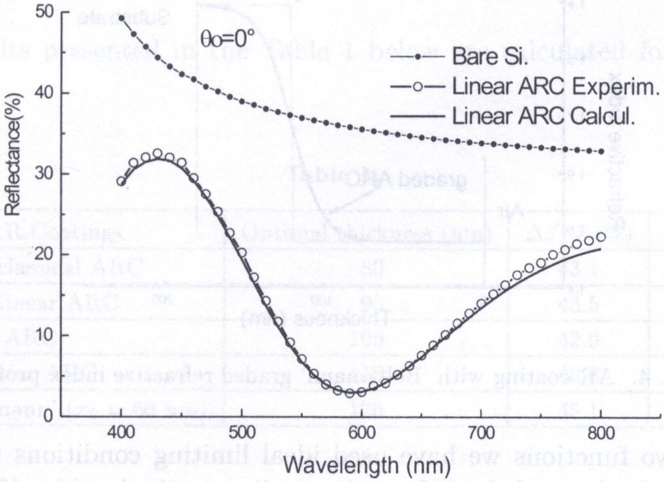

FIG. 3. Réflectance of linear graded AR coating compared to that of bare silicon.

5. OPTIMIZATION RESULTS

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

- To replace a classical mono-layer ARC, we propose a gradient described by the function:

$$f_A = f_0 - (f_0 - f_F)\left(\frac{x}{E}\right)^{\alpha} \tag{5.1}$$

and in order to highlight the influence of index profile on the ARC performances, we have taken three values for α: for a linear profile $\alpha = 1$, $\alpha = 0.5$ and $\alpha = 2$ for supra-linear and sub-linear profiles respectively (Fig. 1).

- To replace a classical double layer ARC, we use a gradient (Fig. 4) described by the following function:

$$f_A = f_0 - (f_0 - f_F)\left[1 + \exp\beta(x - x_0)\right]^{-1} . \tag{5.2}$$

In this expression (Boltzmann function) the parameter β describes the form of the profile ($\beta = 0.2$ in Fig. 4). In the limit condition (β very weak), we obtain the configuration of a classical double layer ARC. Then, the inflection point x_0 represents the silicon nitride thickness.

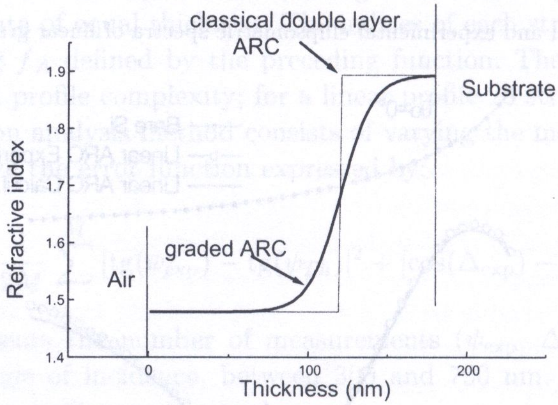

FIG. 4. AR coating with 'Boltzmann' graded refractive index profile.

For the two functions we have used ideal limiting conditions for SiO_2 volume fraction: $f_0 = 1$ and $f_F = 0$, corresponding to the largest refractive index gradient.

The variation of improvement in J_{SC} versus total thickness of ARCs is shown in Fig. 5 for different profiles compared with the classical Si_3N_4 mono-layer ARC. Linear and sub-linear profiles do not seem to be appropriate. The supra-linear profile gives good results: the 6.6% weighted average reflectance and J_{SC} improved by 43.5%. The new 'Boltzmann' profile realizable in a single technological stage permits to improve significantly the performances of graded indices

AR coatings: 5.6% weighted average reflectance and 45.1% improvement in J_{SC}. These results are comparable with those obtained by B.S. RICHARDS *et al.* [7] with classical double layer ARCs.

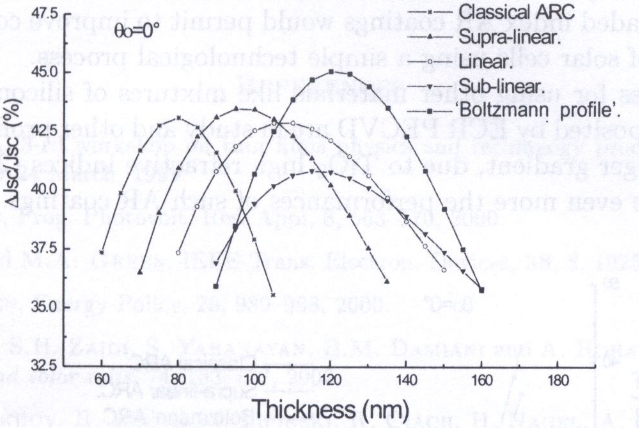

FIG. 5. Improvement of short-circuit current. Graded AR coatings compared to Si_3N_4 classical ARC.

The results presented in the Table 1 below are calculated for normal incidence.

Table 1.

A.R.Coatings	Optimal thickness (nm)	$\Delta J/J$ (%)	R_W (%)
Si_3N_4 classical ARC	80	43.1	7.0
Supra-linear ARC	95	43.5	6.6
Linear ARC	100	42.9	6.9
Sub-linear ARC	115	40.8	8.3
'Boltzmann' ($x_0 = 60$ nm)	120	45.1	**5.6**

Associated with *a priori* texturization of the semiconductor surface, the graded AR coatings will allow to reduce the average reflection to less than a few percent, and will tend to approximate the ideal case (without reflection losses). The improvement of the photocurrent would be: $\Delta J_{SC}/J_{SC} = 53.76\%$.

P. NUBILE [19] proposes that the simplest approach to calculate the reflectivity of a grooved surface is to use the approximate relation:

$$R_{Tex}(\lambda) = [R(\lambda, \theta_0 = \pi/4)]^2 . \qquad (5.3)$$

He considers that in average, the light is reflected twice at the angle of 45°. While replacing the obtained values in the previous expressions of short-circuit current and the weighted average reflectance, we obtained $\Delta J_{SC}/J_{SC} = 52.79\%$ and $R_W = 0.63\%$. This is unquestionably a very good result. In addition, if we take into account the passivation effect of oxynitrides, mentioned by many authors [23–25], the graded index AR coatings would permit to improve considerably the performance of solar cells using a simple technological process.

Perspectives for using other materials like mixtures of silicon and titanium oxides [26], deposited by ECR PECVD are in study and other profiles can be suggested. The higer gradient, due to TiO_2 high refractive indices (2.3 at 500 nm), would improve even more the performances of such AR coatings.

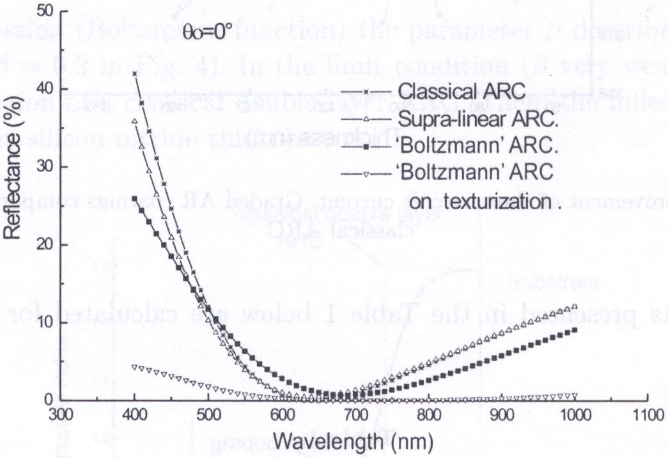

FIG. 6. Reflectance of the best graded AR coatings compared to that of Si_3N_4 classical ARC.

6. CONCLUSION

Silicon oxynitrides graded index antireflective coatings enhance solar cells efficiency by reducing the 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 AR coatings. We can advantageously use passivating oxinitrides with graded index on texturized surfaces. Then, improvement of the short-circuit current of 52.79% and 0.63% weighted average reflection between 300 nm and 1100 nm can practically be obtained. Perspectives of realization of the same type of AR coatings with other materials are in the process of being studied.

ACKNOWLEDGMENTS

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 their technical support.

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Received December 2, 2004.