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Design of porous silicon /PECVD SiO_x antireflection coatings for silicon solar cells

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Abstract.

The meso-poreux porous silicon layer (PS) has become an interesting material owing to its potential applications in many fields including optoelectronics and photovoltaics. PS layers were grown on the front surface emitter n^+ of n^+-p mono-crystalline Si junction. The thickness of the PS formed and the porosity were measured by an ellipsometer as a function of time duration of anodization, and the variation law of the PS growth kinetics is established. Single layers PS antireflection coating (ARC) achieved around 9% effective reflectivity in the wavelength range between 400 and 1000nm on junction n^+-p solar cells. To reduce the reflectivity and improve the stability and passivation properties of PS ARC, the design of PECVD oxide silicon layers were investigated. SiO_x layers of thickness of 105nm deposited on PS ARC showed a decrease of ~3.8% in the effective reflectivity, compared to the single layer PS ARC, improve the reflectivity of 55%. V_{oc} measurements were carried out on all the samples by suns-Voc method and showed an improvement of the quality of the passivation brought by the oxide layer. Using the experimental reflectivity results and taking into account the passivation quality of the samples, the PC1D simulations predict an enhancement of the photogenerated current exceeding 49%.

Keywords: Porous silicon, Silicon dioxide, Antireflection Coating, Photocurrent

1. Introduction

Reducing the front surface reflectance of crystalline silicon (Si) solar cells is one of the most important issues for improving the cells efficiency. Several research groups have used porous silicon (PS) layers as an antireflection coating to reduce the surface reflectance [1]-[4]. The refractive index for PS layers depends on its porosity and its morphology, and the optimization of these factors may lead to an ideal anti-reflection coating for silicon solar cells [5]. Porous silicon possesses other advantages and can also (i) enlarges the spectral sensitivity region [6], (ii) improves photo-generation of carriers [6]-[8], (iii) create simultaneously a selective emitter and an antireflection coating in the same step [6],[9].

However, strong surface recombination related to the roughness of the surface after porous silicon layers formation on n^+ doped emitter of conventional solar cells [10]-[12], and the degradation of its parameters with time if special treatments to preserve the PS properties are not used[13]-[15]. Several treatments have been attempted (rapid thermal oxidation (RTO), nitridation, anodic oxidation, thermal carbonization …) [6],[16]. In this context silicon oxide (SiO_x) films deposited by PECVD on porous silicon surface are of interest, since they have good properties: (i) high chemical stability [16]-[18], (ii) acceptable passivation of the surface after annealing [19],[20],(iii) good antireflection coating (iv) and easy deposition process by PECVD on PS, without deteriorating the optical and structural properties of the underlying PS [17],[21].

This work aims to study the optical and passivation properties of PS and SiO_x/PS combination on n^+/p junction. PS layers were grown electrochemically at a constant current density of 20 mA/cm^2 for different time intervals on the n^+/p junction. The n^+/p junctions were made on (100) P-Si wafers using Phosphorous diffusion from $POCl_3$ source. The SiO_x layers were deposited by RF-PECVD.

2. Experimental

The experiments were carried out on CZ (100) P-type silicon substrates, with resistivity 1-10 ohms.cm. In order to obtain homogenous PS an Al metal layer was evaporated under a vacuum of 10^{-5} mbar on the back side of the sample and was subsequently annealed in air at 750^o C to establish an ohmic contact. The Al contact was connected to a constant current source. PS was grown on the front polished side in a solution of HF (48%) and C_2H_5OH (3:1 and 4:1 in volume) in a Teflon electrochemical anodization solution. A Pt wire was used as a cathode at a distance of 2cm from the Si wafer surface which acted as the anode. In order to grow PS layers with different thicknesses, a set of experiments was performed by using a constant current density of 20 mA/cm^2 for different anodization time: 3.5 to 12 s. The PS wafers have been then cleaned by standard CARO procedure. SiO_x films have been deposited with pure silane and nitrous oxide (SiH_4, N_2O) as precursors gases in a vertical semi-industrial low Frequency PECVD reactor (LF – PECVD) at 440 KHz from SEMCO Engineering (described in [22]). The deposition was made at 370°C, with a power density of 0.26 w/cm^2 and a pressure of 1500 mTorr, and 25 as N_2O/ SiH_4 gas flow ratio equal to 25. The deposition speed is 29 nm/s.

In order to optimize the ARC parameters (optical indexes and thicknesses), the simulation based on the stratified medium theory and the Bruggeman effective medium approximation (EMA) [23], are carried out in the wavelength range between 350 and 1100 nm. The PC1D software was used to estimate the expected values of the photocurrent solar cells [24].

The PS thickness and porosity, and the oxide thickness were measured by a Jobin Yvon Uvisel Ellipsometer, using the Bruggemann effective medium approximation model (EMA) in the range of 1.5 to 5 eV. The total reflectance was measured within the 350 –1100nm wavelength range with an integrating sphere. The effective reflectance is calculated by integrating the reflectivity values balanced by the Sun global irradiance (AM1.5g spectrum). The measurements of the photovoltaic pseudo-parameters (open circuit voltage V_{oc} and pseudo Fill-Factor FF) were carried out with Suns-V_{oc} Stage model WCT-120.

3. Results and discussion

A. Optical results:

1) Porous Silicon layers

Three essential parameters can optimize the antireflection properties of porous silicon: the HF concentration in the ethanol, the current density and the growth Kinetics. In our case two solutions are used: HF (48 %): C_2H_5OH = 3:1 and 4:1 in volume. To adjust the adequate refractive index of the PS, the current density is fixed at 20 mA/cm^2, however the thickness of the layer is controlled by anodization time. Fig. 1 shows that the variation of thicknesses according to the anodization time is exponential in nature, and that the thicknesses are very sensitive to the variations of the anodization time. We can also notice that the average growth kinetics is 14 nm/s. Our calculations showed that the optimum thickness of the antireflection coating (ARC PS) is of 80 nm which corresponds to 6s of anodization.

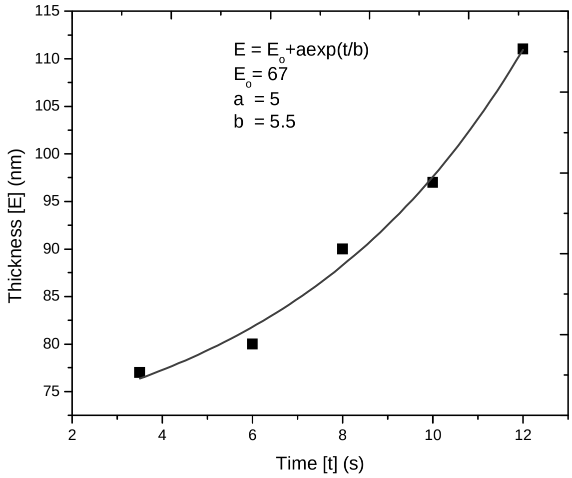

Fig. 1. Thickness E vs time t of PS growth at a constant current density of 20 mA.cm^{-2} on n+ diffused side of (100) Si wafer.

The reflectivity curves of the PS grown on the diffused emitter with a current density of 20 mA/cm^2 and in electrolyte concentrations HF/C2H5OH of 3:1 and 4:1 are represented in Fig. 2. The best reflectance is obtained with the second solution, and presents an effective reflectivity of 9 % with a minimum (R ~ 0) in the wavelength of 650nm. This solution allows to obtain the expected value of porosity which gives exactly the adequate refractive index, leading to the optimization of ARC PS layer. The effective reflectivity compared to that of the standard ARC nitride (R=NH3/SiH4=5) is improved by 1.5 % absolute.

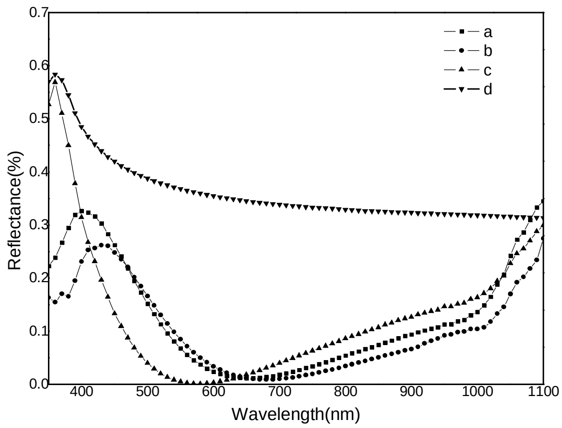

Fig. 2. Total reflectance spectra of : (a) PS growth in HF (48 %): C2H5OH = 3:1, J = 5mA/cm^2, t = 12s; (b) HF (48 %): C2H5OH = 4:1, J = 5mA/cm^2, t = 12s; (c) Standard SiN_x ARC (70nm); (d) Bare polished Silicon.

The Bruggeman effective medium approximation (EMA) is commonly used to determine the refractive indexes of inhomogeneous film [25]-[26]. Using this model, we consider the PS layer as an isotropic physical mixture of two components: bulk Silicon and pores with the dimensions much less than the light wavelength λ [27]. Several autors [7] have caracterized thin porous silicon layer formed in the n+ region in n+/p structure by SEM and AFM, and have obtained the mean size of the pores beteween 20 – 30 nm. This justifies the use of EMA model for ellipsometry analysis. Silicon dioxide (SiO_2) is used for the native oxide present on the surface of the PS [9]. Fig.3 shows that there is a good agreement between the experimental and the theoretical values of reflectivity for 80 nm-thick PS layer with a porosity of 60%, covered by a thin silicon dioxide (SiO_2) layer (5-6 nm). Slight reflectivity increase in the experimental reflectivity spectrum near 1000 nm is due to the reflection on the back side of the wafer (250 µm thick). The spectroscopic ellipsometry (S.E) measurement (Psi and Delta) carried out on these samples, and the fit based on the models proposed by Prabakaran and Strehlke [9,28], confirm a optimum reflectivity adjustment.

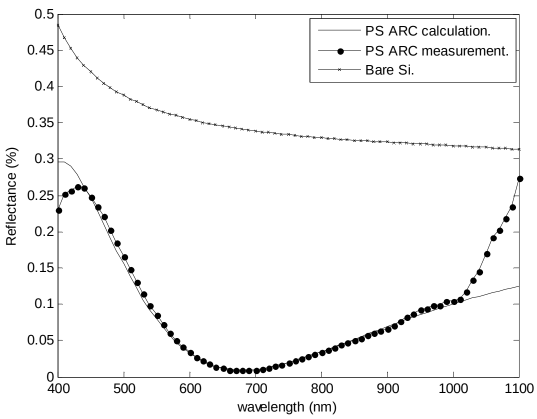

Fig. 3. Calculation and experimental reflectance spectra of PS layer ARC grown on n+/p junction.

2) SiO_x Layers

In order to improve the reflectivity of a single ARC PS, a double PS layer can be grown on the top of the silicon n+/p junction. However this kind of coating can lead to a degradation of the n+ emitter by reducing its thickness, and do not insure a good surface passivation. The deposition of a silicon oxide (SiO_x) layer over the PS layer may be an alternative solution. The silicon oxides deposited in our reactor LF–PECVD present: a large range of refractive indexes (between n=1.47 and n=2 at λ=633 nm), and a very weak absorption in the range 300 – 1100nm. A SiO_x layer can thus be used on the top of the PS layer, to realize refractive index adaptation for antireflection optimization.

The PS layer parameters were fixed at the optimized values (E=80nm, P=60%), and the optical indexes of the SiO_x were determined by spectroscopic ellipsometry. The reflectivity of the double structure PS/SiO_x based on these parameters was computed, and led to different optimum SiO_x thicknesses: 105nm, 90nm, 70nm. The experimental reflectivity curves are presented in Fig. 4. The effective reflectance calculated from the reflectance spectra 400 – 1100nm (inset in Fig. 4), varies linearly as a function of the SiO_x thickness. This result shows that the oxide film thickness of 105nm deposited on PS ARC, compared to the single layer PS ARC, improves the reflectivity of 55%, leading to an effective reflectance of 3.8%.

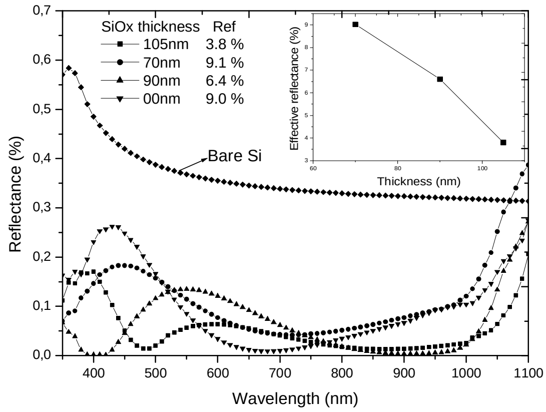

Fig. 4. Reflectance spectra of SiO_x/ PS films on n^+/p junction for various thickness SiO_x (inset of plot : effective reflectance versus different SiO_x layers thicknesses).

S.Sterhlke and co-workers have reduced the effective reflectivity to 2.7 % for double layers PS ARC with a total thickness of 160nm in the range 400 – 1000nm [29]. However such a thickness of PS may risk to degrade the properties of the underlying n+ emitter of the solar cell, which is generally 300 nm-thick. On the other hand the best result obtained in the literature for a double SiN_x/SiO_x ARC layer on polished silicon is Ref = 6.3 % in the range λ=400 -1000 nm [21],[22].

B. Passivation results

We have shown that the reflectivity obtained with PS/SiO_x double layers is good, and can lead to an increase in the photogenerated current. We must then study the effect of such a structure on the electrical performance of the solar cell. The photovoltaic pseudo-parameters V_{oc} and FF obtained with our different structures are presented in Fig 5. The PS layers increase the surface recombination velocity of minority carriers, leading to a large decrease of the V_{oc} compared to a standard silicon solar cell (around 580 mV). The oxide film deposited on PS layers may partly cure leads to a higher Voc, thus leading to an improvement of the surface passivation quality. This improvement can be explained firstly by the presence of the Si-O bonds which passivates the dangling bond within PS. The SiO_x also contains around 4 atomic % of hydrogen [30], which diffuses within the PS-Si layer and increases the number of Si-H bonds which is initially formed during the formation of PS [16], thus enhancing the surface passivation of the pores. The Voc values are thus partly restored, but remain at this point below the reference.

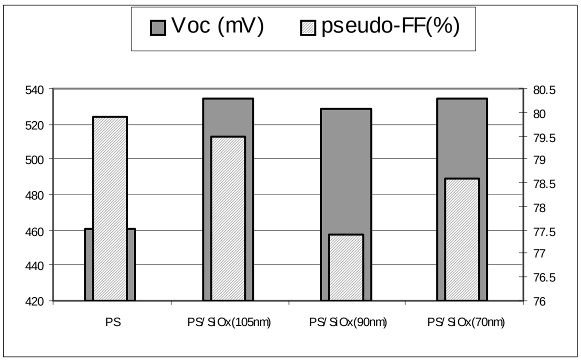

Fig. 5. Parameters suns-Voc obtained in a Junction n+/p with PS and PS/SiO_x as ARC.

C. Photocurrent calculation

Following these results, PC1D [24] program was used to estimate the values of the photocurrent. The experimental reflectivity results of each samples was used in combination with the appropriate values of the front side surface recombinaison velosity (SRV). The photocurrent values presented in the table I are in accordance with the fraction of the photogenerated current in the n+/p junction. The best photocurrent improvement is nearly 49% for the double layer SiO_x/PS ($dSiO_x$=105nm).

Table I

Samples	Ref(%)	Jsc(A/cm^2)	ΔJsc/Jsc(a)	ΔJsc/Jsc(b)
SiN (reference)	9.4	33.1	41.15	-
PS	9.0	33.4	42.73	0.9
PS/SiOx(105nm)	3.8	34.8	48.71	5.13
PS/SiOx (90nm)	6.4	34.1	45.72	3.02
PS/SiOx (70nm)	9.1	33.0	41.02	-0.3

ΔJsc/Jsc was calculated in comparison with: (a)Jsc corresponding to bulk silicon surface (b) Jsc corresponding to reference ARC (SiN).

3. Conclusion

The deposition of the ARC SiO_x on porous layer led to promising results. Investigations of the reflection spectra and the passivation characteristics showed that the optimum results can be obtained with electro-chemical anodization of PS and RF-PECVD of SiO_x ARC layers. Indeed an improvement in effective reflectivity of 55% and the open circuit voltage of 14% is achieved comparing to PS ARC alone. In perspective, the manufacturing of the solar cell with this type of ARC by using the screen-printing technology for the realization of the front contacts can improve effectively the solar cells efficiency.

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