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Feasibility of antireflection and passivation coatings by atmospheric pressure PECVD

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Abstract

An innovative method to obtain antireflection and passivation coatings on p-type crystalline silicon solar cells is presented. The method consists in the growth of hydrogenated silicon nitride films (SiN_x:H) by atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD). Compared to industrial process, using this kind of processing may allow an augmentation of the silicon solar cell production throughput and yield enabling a reduction of the cost of photovoltaic systems. The optical and passivation properties of the SiN_x:H films grown by AP-PECVD are determined and compared with the standard low pressure plasma enhanced chemical vapor deposition (LP- PECVD) films. Minority carrier lifetime of 1 ms was reached. Solar cells coated with AP-PECVD SiN_x:H films were made, and their performances were compared with standard SiN_x:H coated cells. The same cell efficiency is obtained for the two groups of cells proving the interest of the AP-PECVD for the solar cell industry.

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Keywords: p-type silicon; antiflection coating; surface passivation; atmospheric plasma PECVD; in-line coating

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1. Introduction

The potential of the photovoltaic energy to produce a significant fraction of the world energy and to contribute to the reduction of the negative impacts of the fossil fuels is widely acknowledged [1]. However, to become a major energy supplier, photovoltaic energy has still a long way to go in terms of cost reduction, in order to reach grid parity with conventional energies [2]. In this article, we propose a new method to produce antireflection and passivation coatings by atmospheric pressure plasma, which aims to reduce the production cost of silicon solar cells and consequently, the price of the photovoltaic energy.

The usual process to obtain antireflection and passivation coatings on p-type silicon solar cells is the growth of hydrogenated silicon nitride (SiN_x:H) films by low pressure plasma-enhanced chemical vapor deposition (LP-PECVD) using silane (SiH_4) and ammoniac (NH_3) as gas precursors [3]. The major advantage of SiN_x:H films is that they provide both an efficient front surface passivation and have an adequate antireflective behavior [4,5]. Furthermore, during the contact firing inherent to the industrial solar cells processing [6], the hydrogen atoms present in the SiN_x:H film diffuse to the SiN_x:H / Si interface and to the bulk of the sample, reducing the recombination activity of the impurities present in the material, thus performing volume passivation and improving the bulk carrier lifetime [7].

The major drawback of these types of methods is the use of low pressure plasma which demands (i) time consuming steps like pumping and filling the reactor, (ii) batch processing that limits the solar cell production rate (iii) wafer handling leading to wafer breaking.

In the new method proposed here, the SiN_x:H films are grown by atmospheric pressure plasma enhanced chemical vapor deposition (AP-PECVD). The use of this kind of processing, instead of a low pressure one, not only allows an augmentation of the solar cell production throughput but has also the potential to increase the yield due to the elimination of handling during wafer loading and unloading steps. Finally AP-PECVD processes have the important benefit of being compatible with a fully in-line solar cell processing [8].

In this article, optical and passivation properties of SiN_x:H films grown by AP-PECVD are presented and compared to LP-PECVD ones. In addition, p-type monocrystalline silicon solar cells, using AP-PEVCD films as antireflection and passivation coatings, were made and their performances were compared with reference cells coated with standard LP-PECVD SiN_x:H films.

2. Experimental details

Film growth details and solar cell processing are first described, the methods used to characterize SiN_x:H films and solar cells are then introduced.

2.1 Film growth

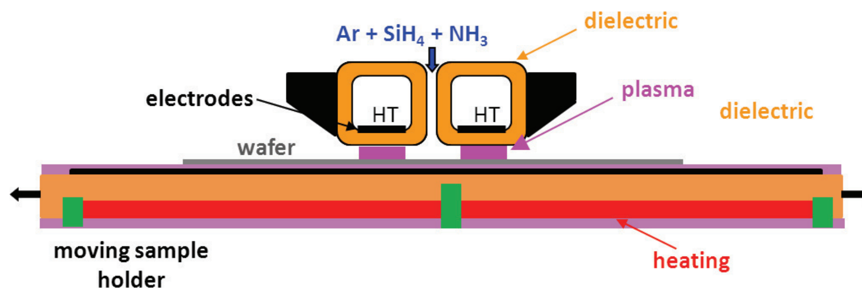

Fig. 1. Schematic view of the plasma reactor.

SiN_x:H films are grown on p-type and n-type Czochralski (Cz) silicon wafers, with a resistivity between 1 and 10 Ω.cm. Before starting the film growth processing, wafers are etched in a 5% hydrofluoric acid (HF) solution to remove the native oxide and then rinsed with high purity water (ρ ~18 MΩ). The silicon wafers are then inserted in the AP-PECVD reactor (Fig. 1).

The gas mixture is composed of ammoniac (NH_3) and silane (SiH_4) as reactive gases, and argon (Ar) as vector gas. Those gases are injected between the dielectric square bars, reaching the zones under the dielectric bars where the plasma is created and the film growth occurs. The two plasma zones (pink) are defined by the electrical metallization of the lower inner face of the dielectric bars. When the substrate is static, only the parts which interact directly with the plasma are coated. To obtain homogenous coatings over all the surface of the samples, a translation system moves the sample holder back and forth with a defined speed.

During this work, an argon flow of 6 l/min is used. The sum of reactive gases flows $[NH_3] + [SiH_4]$ is 200 ppm and the ratio, $R = [NH_3] / [SiH_4]$, is adjusted between 1.74 and 1.85. The pressure is always equal to 1 Bar. The film growth temperature is 400°C. The plasma excitation conditions were varied: frequency is tuned between 50 kHz and 7300 kHz and modulated or not by a square signal having a period of 5 ms. Further details on the growth method can be found in [9, 10, 11].

To perform the SiN_x:H film characterization, n-type and p-type polished Cz silicon wafers with 2.6 Ω.cm, were used as substrates.

To analyze the effect of the contact firing performed during the standard industrial solar cell processing, the SiN_x:H films were submitted to a rapid thermal annealing (RTA) in nitrogen with a peak temperature of 790 °C (Fig. 2) in a JETFIRST Jipelec furnace oven, after which the characterization was repeated.

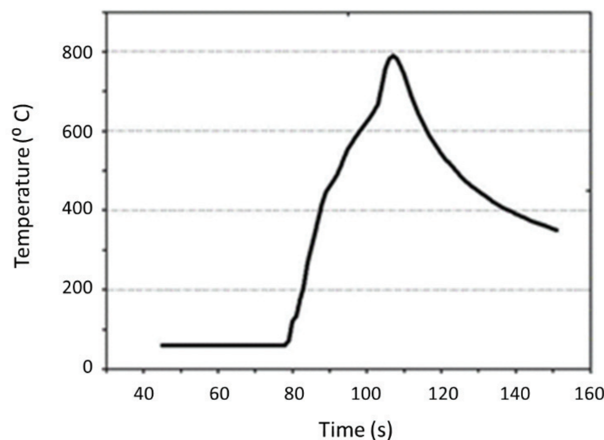

Fig. 2. Rapid thermal annealing temperature profile.

2.2 Solar cell processing

After the characterization of the AP-PECVD films, the growth conditions that showed the best optical and passivation behavior were used to fabricate solar cells (2×2 cm^2) on 160 μm thick, p-type Cz silicon textured substrates. The textured substrates were submitted to a phosphorous diffusion to form the emitter, 65 Ohm/sq. Then, the SiN_x:H films were grown on the front surface; two groups of cells were made: one with AP-PEVCD grown SiN_x:H and the other with a standard low pressure grown SiN_x:H film. Both groups underwent the same metallization procedure that included: the formation of the back contacts by aluminum (1 μm) evaporation; wet etching of the SiN_x:H film after photolithography steps and evaporation of titanium (40 nm), palladium (40 nm) and silver (1 μm) to form the front contacts. Finally the solar cells went through an annealing step during 40 s at 450 ºC, to ensure a good ohmic contact. The solar cell processing did not include back surface field formation.

2.3 Characterization

SiN_x:H films chemical compositions were determined by Fourier transformed infrared (FTIR) spectrometry, using a Nicolet 6700 spectrometer in transmission mode, in the 650 - 4000 cm^{-1} range. Film thickness and optical properties were determined by spectroscopic ellipsometry measurements in the range 430 to 850 nm, using a Jobin-Yvon MM-16 spectroscopic ellipsometer. To examine the conformity of AP-PECVD SiN_x:H films grown on textured substrates, the reflectivity of textured Cz silicon substrates coated with AP-PECVD was measured and compared with textured substrates coated with standard LP-PECVD SiN_x:H films.

Passivation properties were obtained by measuring the effective minority carrier lifetimes (τ_{eff}) with a Sinton WCT-120 wafer lifetime tester on Quasi-Steady-State and transient modes. To analyze the effect of the contact firing step, the SiN_x:H films were submitted to a rapid thermal annealing (RTA), after which the characterization was repeated.

Solar cell one-sun IV curves were obtained with a Sinton Light I-V Testing FCT-400 and the fundamental solar cell parameters were determined. Dark-IV curves were also measured and the saturation currents I_{01} and I_{02} were determined for all the cells. The solar cells reflectivities and spectral responses were measured, and the internal quantum efficiency (IQE) obtained.

3. Results and discussion

3.1 Chemical and optical properties

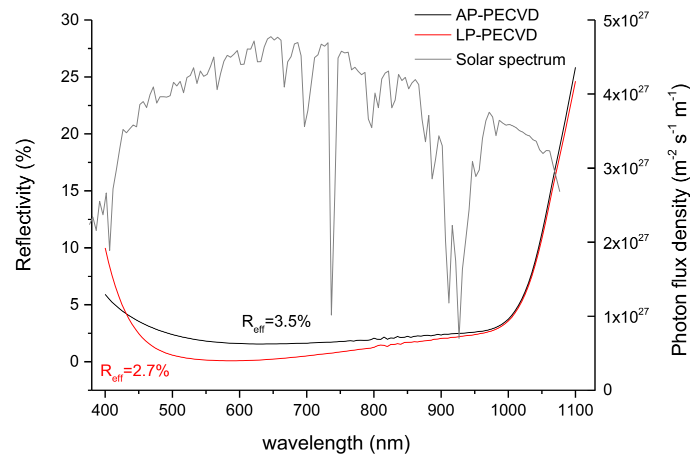

Fig. 3. Effective reflectivity for AP and LP SiN_x:H films

The FTIR measurements performed on AP-PECVD SiN_x:H films reveal the same type of chemical bonds than those obtained for LP-PECVD films [12,13], which indicates that AP- and LP- PECVD SiN_x:H films have similar chemical compositions.

The ellipsometry measurements showed that, similarly to LP-PECVD films, the optical properties of AP-PECVD SiN_x:H films can be tuned by varying the gas composition of the plasma. Namely the film refractive index, n, is augmented by decreasing the ratio of NH_3/SiH_4 and an increase of the extinction coefficient k is observed for $n > 2.1$ [13]. In order to avoid significant light absorption by the SiN_x:H films [14], the films studied during this work have refractive indexes n~2.1 and negligible extinction coefficients k.

Although the ability to grown AP-PECVD SiN_x:H films, on polished monocrystalline silicon substrates, with similar chemical and optical properties as the ones obtained with LP-PECVD has been demonstrated [11,13], it can

be observed (Fig. 3) that the effective reflectivity of textured monocrystalline silicon wafers coated with AP-PECVD SiN_x:H films is 3.5%, compared with 2.7% for the LP-PECVD SiN_x:H coated wafers. This difference is attributed to a lack of coating conformity on silicon pyramids. As illustrated in Fig. 4, the thickness of the film is thicker on the top of the pyramid than on the bottom. The higher is the pyramid the larger is the difference. This is related to the low mean free path of reactive species in a gas at atmospheric pressure and to the high reactivity of SiH_4 radicals.

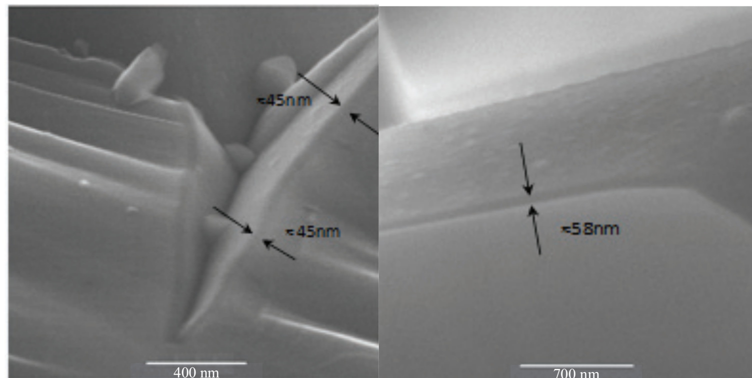

Fig. 4. SEM image of a silicon slice showing that the coating is thinner on the bottom (a) than on the top (b) of a pyramid of a textured wafer.

Such difference on the reflectivity should imply a loss of nearly 1% in the short-circuit current of the AP-PECVD SiN_x:H coated solar cells, when compared to LP-PECVD SiN_x:H coated ones.

3.2 Passivation behavior

The effective lifetimes τ_{eff} of n-type Czochralski silicon wafers ($\rho = 2.6\ \Omega$.cm) passivated with AP-PECVD SiN_x:H films, using different plasma excitations are presented in Fig. 5. Two parameters have been varied: the plasma frequency and the plasma modulation for a given plasma frequency. In Ar/NH_3/SiH_4 at atmospheric pressure, frequency drastically changes the plasma characteristics [15] from 50 kHz to 9 MHz. Up to 250 kHz, ions drift to the electrodes and contributeto the coating. The electron density is intermediate and their energy is rather high. The main ion, NH_3^+, directly contributes to the thin film chemistry. From about 1 MHz, for a 1 mm gas gap, electrons begin to be trapped in the gas leading to the radiofrequency plasma mode associated to a high density of low energy electrons. Between 250 kHz and 1 MHz the discharge is a Townsend discharge in which the electron energy is high and their density low. One of the consequences of the variation of the plasma physics is that the ratio of NH_3/SiH_4 leading to a refractive index of 2.1 varies with the plasma frequency. It depends on how much the NH_3^+ ions contribute to the coating. The values of gas ratio used to prepare the coatings for the passivation study are summarized in table 1. The lower ratio of NH_3/SiH_4 corresponds to the glow discharge, i.e. when NH_3^+ ions largely reach the substrate.

Table 1. Conditions leading to a refractive index of 2.1 and corresponding to the passivation results presented in Fig. 5.

Frequency	R=[NH3]/[SiH4]	Discharge regime
50 kHz	1.47	Glow discharge
200 kHz	1.47	Glow discharge
500 kHz	1.65	Townsend discharge
900 kHz	1.7	Mixed Townsend and radio frequency
7.3 MHz	1.7	Radio frequency discharge

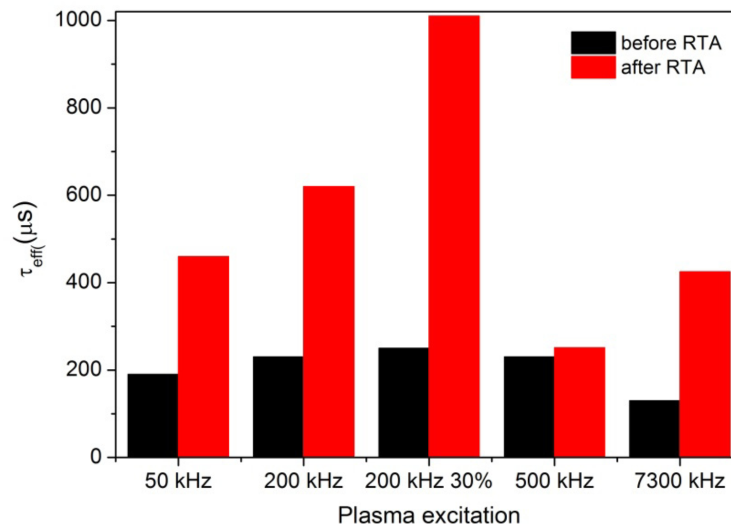

Fig. 5. Effective lifetime, τ_{eff} as function of the plasma excitation (n-type, Cz Silicon).

The minority carrier lifetime measurements performed on polished monocrystalline silicon wafers (n-type and p-type) showed that AP-PECVD SiN_x:H films attain a good surface passivation. Plasma modulation largely improves the surface passivation.

Fig. 5 shows that for all conditions tested τ_{eff} increases after RTA. Moreover SiN_x:H films grown with a plasma frequency f = 200 kHz and square-wave modulation with frequency 200 Hz and duty cycle $T_{on}/(T_{on}+T_{off})$ = 30% have the best passivation behavior achieving τ_{eff} = 1 ms after RTA.

The large influence of the plasma modulation is explained by a significant improvement of the chemistry uniformity [14]. As the gas is introduced on one side of the plasma, its chemical composition evolves with the discharge interaction. The concentration of SiH_4 and NH_3 decreases exponentially while secondary products are formed. The consequences of this gas chemistry evolution on the surface passivation have been studied on static samples (samples made without moving the substrate holder) using Semilab µPCD cartography. Before thermal annealing, passivation is best at the plasma entrance, where hydrogen concentration is higher while after thermal annealing, passivation is better where the film thickness is maximum which is in agreement with the literature [16].

In general, modulation reduces the precursor dissociation. However, as their concentration is always rather high, the chemistry is not affected by the lack of precursors, and the films are homogeneous all over the substrate. Furthermore, the coating covers a larger surface.

After finding the appropriate AP-PECVD processing parameters to obtain high quality antireflection and passivation coatings, these conditions were used to fabricate solar cells.

3.3 Solar cell characterization

Solar cells made on paired mono-crystalline silicon wafers, in a similar manner except for the type of the SiNx:H deposition (AP- and LP-PECVD) and their performances compared. In Fig. 6 the comparison of the current-voltage characteristics of AP- and LP-PECVD coated solar cells is presented, the similarity of the two curves is obvious.

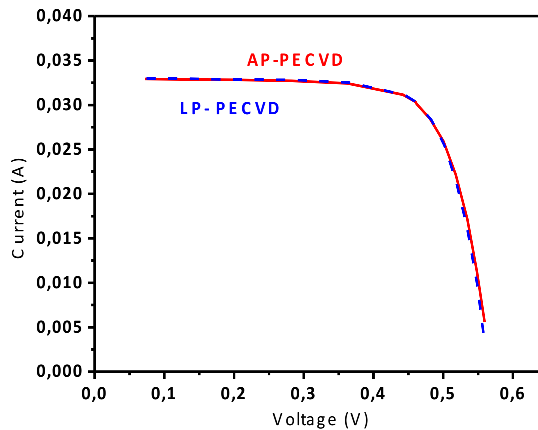

Fig. 6. Current voltage characteristics of AP- and LP- PECVD coated cells

Table 2 presents the solar cell parameters for the three best AP- and LP- PECVD cells. Results are very similar. AP-PECVD solar cells have a lower short-circuit density J_{sc}, than LP-PECVD ones, such result is mainly a consequence of the higher effective reflectivity of the AP-PECVD coated wafers.

The open-circuit voltage (V_{oc}) and fill factor (FF) are slightly higher for AP-PECVD cells proving that AP-PECVD SiN_x:H films accomplish a correct surface passivation.

Table 2. Solar cell parameters for the best three cells

Cell type	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)	J_{01} (pA/cm^2)	J_{02} (µA/cm^2)
AP-PECVD	567.4±1.8	32.8±0.8	73.8±1.8	13.8±0.7	10.9±0.9	(3.2±2.2)×10^{-2}
LP-PECVD	564.8±0.1	33.4±0.3	72.9±1.8	13.7±0.7	11.7±1.7	(6.3±5.0)×10^{-2}

It is interesting to point out that the solar cell efficiency is nearly the same for the two sets of cells, showing that on the overall AP-PECVD SiN_x:H passivated solar cells have an equivalent performance as solar cells with the standard SiN_x:H passivation. Also, the saturation currents, J_{01} and J_{02} for the AP-PECVD cells not only are of the same order of magnitude than the LP-PECVD ones, but are even slightly lower. Such result confirms that AP-PECVD SiN_x:H films provide a good passivation of both the surface and the volume of the solar cells. The values

of J_{01} and J_{02} obtained for both groups of cells (AP- and LP-PECVD) are significantly higher than for standard monocrystalline silicon industrial solar cells [6]. This result can in part be attributed to the absence of a back surface field [17]. The values of J_{01} and J_{02} can explain part of the losses on V_{oc} and FF [17] and consequently, the relatively low conversion efficiencies of the solar cells.

Internal quantum efficiency (IQE) curves for one cell of each group (AP- PECVD, LP- PECVD) are presented in Fig. 7. The great proximity of the curves in the blue region confirms that the two passivation schemes perform in a similar way, confirming the quality of AP-PECVD SiN_x:H passivation. Furthermore, the coincidence of the two curves in the near infrared confirms the good volume passivation provided by the AP-PECVD SiN_x:H films.

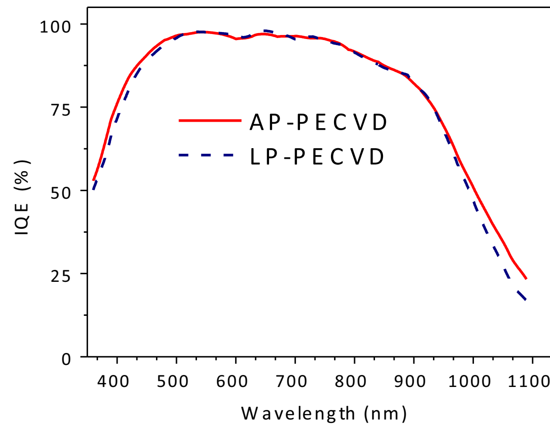

Fig. 7. Internal quantum efficiency of AP- and LP- PECVD coated solar cells

4. Conclusions

A new method to obtain the passivation and antireflection coating of p-type silicon solar cells, based on the growth of SiN_x:H by atmospheric pressure plasma was developed.

SiN_x:H films obtained by AP-PECVD show the same chemical and optical properties when grown on polished substrates. However, the effective reflectivity of textured substrates coated with AP-PECVD SiN_x:H films is higher (R_{eff}=3.5%) than for substrates coated with LP-PECVD (R_{eff}=2.7%). Such difference implies a small loss of the AP-PECVD solar cells short-circuit current, a lower J_{sc} is indeed observed for the AP-PECVD solar cells. Open-circuit voltage and fill factor is slightly higher for AP-PECVD than for LP-PECVD cells, proving the quality of the surface and volume passivation provided by AP-PECVD SiN_x:H films. This is confirmed both by the saturation current values and internal quantum efficiencies of the solar cells.

Overall AP-PECVD solar cells have the same efficiency as LP-PECVD cells. To our knowledge it is the first time that atmospheric pressure plasma grown SiN_x:H films achieve the same performance as standard low pressure PECVD SiN_x:H ones. Given the important benefits of replacing low pressure PECVD by atmospheric pressure plasma PECVD such result may have an important impact on the PV industry.

Acknowledgements

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