A comparative study of the electrical characteristics of solar cells passivated with a double layer of SiN_x/SiO₂ and a single layer of SiN_x

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Abstract— The double-layer passivation of silicon nitride on silicon oxide (SiN_x/SiO_2) represents a promising avenue for the mitigation of potential induced degradation (PID) in photovoltaic (PV) modules. The objective of our research is to develop and analyse solar cells with a double layer of SiN_x/SiO_2 . Subsequently, the electrical parameters are compared to those of conventional solar cells, which have been treated with a single layer of SiN_x as an anti-reflective coating. The findings obtained through the utilisation of a solar simulator and the Qss-Sun V_{oc} illustrated that the layer of SiN_x/SiO_2 resulted in enhanced passivation characteristics, exhibiting an open circuit voltage V_{oc} 98% higher than the cells passivated with a single SiN_x layer. With regard to the fill factor (FF), the SiN_x/SiO_2 passivation recorded 80%, versus 73.2% for the cells with a single layer SiN_x .

Keywords—SiN_x/SiO₂, passivation, solar cells, Silicon.

I. INTRODUCTION

The surface of the silicon wafer represents the primary source of recombination centres and, as a consequence, requires passivation. An effective surface passivation process will result in a low surface recombination velocity, which will contribute to an enhancement of the effective lifetime. In the present era, particular attention is granted to the quality of passivation achieved through the deposition of dielectric layers [1]. It is therefore evident that surface passivation represents a crucial element in the translation of high-efficiency crystalline silicon solar cell concepts into industrial production schemes [2]. Among the various techniques employed for the purpose of enhancing the efficiency of solar cells, the double layer $H-SiN_x/SiO_2$ deposition stands out as a particularly effective approach. This method offers the dual benefit of providing both surface and bulk passivation. The SiO₂ film, in particular, has been shown to exhibit field effect passivation [3, 4], while the SiN_x contributes to chemical passivation [4, 5]. The hydrogen present in silicon nitride serves to guarantee the effectiveness of the bulk passivation. In 1997 Nagayoshi et al. [6] conducted his works into H-SiN_x/SiO₂ double layer passivation with Hydrogen radical annealing for solar cells; and states that the effective lifetime was markedly enhanced by the introduction of a SiN_x:H/SiO₂ double-layer passivation structure in lieu of a SiN_x:H or SiO₂ single-layer; The authors also state that the capacitance-voltage measurement indicate the presence of a significant number of positive charges within the SiN_x:H layer. The combination of field effect by these charges and the reduction of SiO₂/C-Si interface defects through hydrogenradical annealing effectively reduce the surface recombination velocity.

Furthermore, the utilisation of a SiN_x/SiO_2 double stack in silicon surface passivation presents a promising avenue for the reduction of potential induced degradation (PID), which is a significant factor contributing to power loss in photovoltaic systems based on crystalline silicon [7].

A substantial body of research has been conducted to date investigating the electronic quality and Czochralski (Cz) defects in silicon using a thin layer of thermally grown SiO₂ and different dielectric capping layers deposited by means of plasma-enhanced chemical vapor deposition (PECVD) and atomic layer deposition (ALD) [8].

This contribution presents an elaboration and characterisation of Al-BSF solar cells with double stack SiN_x/SiO_2 passivation. Subsequently, a comparative study of the electrical parameters was conducted between conventional solar cells using single layer surface passivation with SiN_x and the cells elaborated around a double layer passivation H-SiN_x/SiO₂ (silicon dioxide (SiO₂) / hydrogenated silicon nitride (SiN_x)).

To assess the electrical parameters of the devices, we carried out the QSS-Sun V_{oc} measurements and the solar simulator characterisation. The results demonstrate that the double passivation layer comprising SiN_x/SiO_2 exhibited a 98% improvement in passivation efficacy compared to cells utilising a single SiN_x layer. Additionally, an optical characterisation has been conducted utilising a Carry 500 Varian spectrophotometer.

II. EXPERIMENTAL PROCEDURES

In this experimental section, we built solar cells on p-type Cz <100> monocrystalline silicon with a resistivity of 1-3 Ω cm, passivated with a SiNx/SiO₂ double layer. To achieve this, each step of the technological process was subjected to electrical and/or optical characterization. The technological process adopted, begins with the surface treatment of silicon wafers, followed by the fabrication of an n⁺/p emitter. A SiNx/SiO₂ dielectric layer is then deposited, followed by metallization of the front and rear faces, and then annealing of the contacts.

A. Chemical surface treatment of silicon wafers

The initial thickness of the wafers used in this study is around 410 μ m. The first step in the PV cell technological process consists of cleaning the surface in chemical baths to remove impurities and undesirable particles such as dust, resins, and oils, as well as crystalline defects induced by mechanical stress during the wafer cutting stage. For this reason, the chemical treatment we carried out before producing the n+/p emitter can be summed up in three stages: degreasing, thinning, and stripping of the silicon oxide layer (SiO₂), known as native oxide.

✓ Degreasing

This stage removes organic matter: grease, wax residues, and dust particles deposited on the sample surface using a bath of trichloroethylene $C_2H_3Cl_3$ (TCE), followed by a bath of acetone and then isopropyl alcohol. The sample is then rinsed with deionized water of very high resistivity (18 M Ω) and dried under a stream of dry nitrogen. These steps are described in the following chronological order:

- Trichloroethylene (TCE): 80°C, 10 minutes.
- Acetone: 2 minutes at room temperature.
- Isopropyl alcohol: 1 minute at room temperature.
- (deionized water) rinse and nitrogen drying

✓ Slimming-Polishing

Next comes the thinning-polishing step, performed in a NaOH bath at a temperature of 85°C. To achieve this, we prepared a 30% NaOH solution, then immersed the wafers in this bath for 10 to 12 minutes to remove around 40 μ m from each side. This step is followed by neutralization in an HCl bath, which neutralizes the Na+ ions from the thinning step, which are harmful due to their recombination activity on the surface. This treatment is followed by a thorough rinse with deionized water and drying under a stream of nitrogen. At the end of this stage, final wafer thicknesses measured with a digital palmer are of the order of 340 μ m. It should be noted that, in addition to thinning the wafers, this treatment also polishes the surface, thereby eliminating mechanical surface defects caused by cutting the briquettes into wafers.

✓ Native Oxide Stripping (SiO₂)

Before moving on to phosphorus doping or measuring minority carrier lifetime using the QSSPC technique, the wafers are treated in a hydrofluoric acid (HF) solution to remove the native oxide layer since the silicon surface is highly reactive with oxygen in ambient air. At the end of these steps, the wafers are rinsed with deionized water and

dried under dry nitrogen in the spin dryer. The operation lasts 9 minutes at a rotation speed of 3500 RPM under nitrogen.

B. Formation of an n^+/p emitter using diffusion process:

The n^+/p emitter is formed in a diffusion furnace of Semco-engineering from a liquid source of phosphorus oxychloride (POCl₃) at a temperature of 820°C with a pressure of 150 mbar. The chemical reactions involved in this step commonly named the pre-deposition step are described by [9]:

$$4\text{POCl}_{3}(l) + 3\text{O}_{2}(g) \rightarrow 2P_{2}\text{O}_{5}(l) + 6\text{Cl}_{2}(g)$$
(1)

In the diffusion phase, phosphorus (P) diffuses from the surface to the bulk of the wafers upon reduction of P_2O_5 by silicon atoms, in accordance with the following equation:

$$2P_2O_5(l) + 5Si(s) \rightarrow 5SiO_2(s) + 4P(s)$$
⁽²⁾

The P_2O_5 layer on substrates is typically designated as phospho-silicate glass (PSG). The diffusion of phosphorus atoms released from the PSG layer into the bulk of the wafers is referred to as the drive-in step. The phenomenon of diffusion is governed by the Fick laws [9]:

$$\frac{\partial}{\partial t}C(x,t) = \frac{\partial}{\partial x}\left(D\frac{\partial}{\partial x}C(x,t)\right)$$
(3)

Where D is the diffusion coefficient, C is the dopants concentration.

It is important to note that the process adopted enables the attainment of a sheet resistance of 55 ohm per square.

C. Oxidation followed by SiNx deposition:

A conventional thermal oxide (CTO) with a thickness of 10 nm was meticulously formed in a quartz tube furnace manufactured by SEMCO-Engineering. This process involved the utilisation of a controlled N_2/O_2 gas flow at a temperature of 800°C for a precise duration of 13 minutes. The formation of the thermal oxide layer is a critical step, as it serves as a passivation layer that significantly reduces surface recombination velocities, thereby enhancing the overall efficiency of the solar cells.

Following the formation of the CTO layer, a 70-nm silicon nitride (SiNx) film with a refractive index of 2.0 was deposited on the oxidised samples. This deposition was carried out using plasma-enhanced chemical vapour deposition (PECVD), a technique known for its ability to produce high-quality films with excellent uniformity and control over film properties. The deposition process utilised ultrahigh-purity silane (SiH4) and ammonia (NH3) precursor gases. The NH3/SiH4 ratio was maintained at 7.44, ensuring the optimal stoichiometry for the SiNx film. The PECVD process was conducted under a microwave power of 4600 W and a pressure of 0.2267 kPa, conditions that are carefully chosen to achieve the desired film characteristics, such as low hydrogen content and high density.

The combination of the CTO layer and the SiNx film plays a crucial role in the performance of the solar cells. The CTO layer provides excellent passivation, while the SiNx film acts as an anti-reflective coating, reducing the reflection of incident light and thereby increasing the amount of light absorbed by the solar cell. This dual-layer structure is essential for achieving high-efficiency solar cells, as it enhances both the electrical and optical properties of the device. [10,11].

D. Laser Edge Isoation:

A short circuit results from the emitter's elaboration, which forms a parasitic junction near the wafer edge. This connection is removed using a cylindrical plasma reactor. Wafers are inserted, carbon tetrafluoride (CF4) is ionized, and high-frequency electric discharge is used in the reactor. A plasma is created when this ionization breaks down into reactive species. There is a reaction involved that is as follows:

$$4F^- + Si \longrightarrow SiF_4 /$$
 (4)

Silicon tetra fluoride, a volatile gas, is created when fluoride and silicon combine. The two emitters that were created on the two sides of the wafer are isolated at the conclusion of this stage

E. Metallization: screen-printing of collector grid and rear contact

The metal contacts of the emitter and substrate are used to collect the photogenerated carrier current. The contacts must be Ohmic, i.e. the I = f(V) characteristic of the contact must be linear. Contact resistance is a very important parameter, and a high resistance value increases the cell's series resistance, lowering its form factor and efficiency. Different processes are used to make contacts.

In industrial photovoltaic cells, contacts are generally screen-printed. [12]

To increase productivity, the front and rear metal contacts are jointly heat-treated. Consequently, handling the cells on the production line requires the following preliminary steps, which we performed scrupulously during the course of our work:

• Screen printing of the back contact (Al) followed by drying in a conveyor oven at 250°C for five minutes to allow evaporation of the solvents.

• Screen-printing of the front collector grid (Ag) onto the SiN_x anti-reflective layer was also followed by 5 minutes of drying at a temperature of 250 °C.

• Simultaneous annealing in an RTP rapid annealing furnace.

 \checkmark Back side: the contact is deposited over the entire surface. As aluminum is a doping element for p-type silicon, it will enable the creation of a p⁺/p back field, known as BSF (Back Surface Field), during metallization annealing.

 \checkmark Front side: the contacts have been deposited with a silver paste through a grid, consisting of 43 thin fingers connected by two 2mm-wide bus-bars. The choice of silver on the front panel is based on the physics of metal-semiconductor contact, where silver produces an ohmic contact with n-type silicon. A contact finger width of 100 µm and a height of 5 to 10 µm increase the active absorbing surface, with a shading factor < 10% of the total surface and minimal series resistance Rs [13].

After deposition of the paste, followed by drying as described above, a rapid annealing step was subsequently carried out, during which contacts were formed on both sides of the wafer. Annealing was carried out in a rapid annealing furnace (RTP): a temperature plateau at 500°C enabled the formation of the BSF on the rear face (formation of an Al-Si phase), followed by a temperature peak at around 800°C for a few seconds, ensuring the formation of the ohmic contact on the front face.

III. RESULTS AND DISCUSSION

A. Measurement of the resistivity of post-diffused Si-mono wafers using the four-point probe method:

The four point probe method is one of the methods dedicated to measuring the resistivity (ρ) of a conductive or semiconducting layer of thickness "e". We conducted our study using an automatic resistivimeter, enabling us to customize the mapping of measurement points based on the number of points and their placement on the surface. This measurement therefore provides a distribution of R \square values, giving a percentage order of R \square uniformity. In our case, we chose 9 points across the surfaces of the wafers studied. Figure 1 illustrates the values of the square resistances measured after formation of the n⁺/p emitter obtained on one sample among the wafers studied.

So, as we can see, the average surface resistance R_{\Box} for the nine measured points is 55 ohms per square with a uniformity of 3%, which suggests a junction depth of about 0.6 microns.



Fig 1: Resistivity assessment by means of the 4 point probe measurements on the substrates after emitter realisation

B. Measuring the lifetime of electric charge carriers:

In order to characterize our wafers in terms of passivation quality, QSSPC measurements were carried out on $SiO_2/n^+p/p$ -Si samples: (As-cut) wafers (black curve) are non-diffused and non-oxidized samples; post-diffused wafers (red curve) and diffused+SiO₂ wafers thermal at 850°C (blue curve) are wafers with an n⁺/p emitter that have undergone thermal oxidation. Figure 2 shows the experimental results obtained by QSSPC, representing the evolution of the effective lifetime τ_{eff} (µsec) as a function of the carrier injection level Δn .



Fig 2: Effective lifetime τ_{eff} as a function of injection level Δn of SiO₂/n⁺p/p-Si samples measured by QSSPC.

From Fig. 2, measurements of the minority charge carrier lifetime show that we have an improvement in τ_{eff} after phosphorus diffusion, a result that was to be expected as phosphorus has a getter effect on transition metals. After deposition of the SiO₂ layer, τ_{eff} recorded very interesting values of around 95 µs. So we can say that SiO₂

has fully played its role in passivating the surface. The addition of the SiN_x layer will only enhance the quality of the passivation due to its high hydrogen content.

The next step was to check that this SiN_x/SiO_2 double layer was suitable for photovoltaic applications in terms of reflectance, since for a layer to be suitable for solar applications, it must absorb a maximum at a wavelength of around 600 nm - the maximum wavelength in the solar spectrum. It's worth noting that the simple SiN_x layer has been extensively studied by scientists in the community.

C. The reflectance characterisation:

The reflectance characterisation demonstrates that both cells, passivated with a single layer of SiN_x and a double layer of SiN_x/SiO_2 , exhibit favorable performance with a minimum reflectance at ~ 600 nm, as illustrated in Figure 3.



Fig.3: Reflectance characteristic of the solar cells with double and single passivation layer.

D. The electrical characterisation:

The study on the solar cells produced was conducted using an ORIEL solar simulator. The standard measurement conditions, namely a light intensity of 1000 W/m² and a temperature of 25°C, were applied using the AM1.5G spectrum. Before starting the measurements, the instrument was carefully calibrated using a calibration cell to ensure the accuracy of the results.

The electrical characteristics of the cells fabricated in our project show remarkable performance. In particular, the cells passivated with a double layer of SiN_x/SiO_2 exhibit superior short circuit current (I_{sc}) and open circuit voltage (V_{oc}) compared to those passivated with a single SiN_x layer. These results indicate that the double passivation layer improves the efficiency of the solar cells by reducing charge carrier recombination and increasing light collection.

The results obtained are presented in Table 1, which clearly illustrates the advantages of the double passivation layer in terms of electrical performance. These findings are promising for the development of more efficient solar cells and could have significant implications for the photovoltaic industry.

TABLE I
A comparative analysis of the electrical parameters of cells passivated with double-layer SiN_x/SiO_2 and those passivated with single-
LAYER SINX

Cells passivation	I _{sc} (Amp)	V_{oc} (mV)	FF
SiN _x /SiO ₂	2.17	606	54
SiN _x	1.96	599	46.6

In consideration of these findings, it can be posited that the gain with respect to the short-circuit current (I_{sc}) is 9.68%, and with respect to the open-circuit voltage (V_{oc}), it is 1.16%. This indicates a notable improvement in the electrical performance of the solar cells, which is crucial for enhancing their overall efficiency.

Nevertheless, the fill factor remains low, which can be attributed to elevated series and parallel resistance, as evidenced by a detailed examination of Table 1. This phenomenon typically culminates in inadequate metalsemiconductor contact and the emergence of leakage currents, largely due to the RTP annealing process (high silver penetration, resulting in junction breakthrough). The high series resistance can impede the flow of current, while high parallel resistance can lead to significant power losses, both of which are detrimental to the cell's performance

To gain a more accurate understanding of the passivation quality, a characterisation of open circuit voltage, which is the fingerprint of the passivation quality and the fill factor, was conducted using the QSS-Sun V_{oc} technique. This characterisation provides the electrical parameters of a cell, excluding the impact of series resistors.

By isolating the effects of series resistance, the QSS-Sun V_{oc} technique allows for a clearer assessment of the intrinsic properties of the passivation layer and its effectiveness in reducing recombination losses.

It is important to note that the I_{sc} values injected in QSS-Sun V_{oc} manip are identical to those provided by the solar cell simulator. This consistency ensures that the data obtained from the QSS-Sun V_{oc} measurements are directly comparable to the simulated values, providing a reliable basis for evaluating the performance of the solar cells. The resulting data are presented in Table 2, which highlights the key electrical parameters and their implications for the overall efficiency and stability of the solar cells.

Furthermore, the detailed analysis of the QSS-Sun V_{oc} data can reveal insights into the potential areas for improvement in the fabrication process. For instance, optimizing the RTP annealing conditions to minimize silver penetration and junction breakthrough could significantly enhance the fill factor and overall performance of the solar cells. Additionally, exploring alternative passivation materials or techniques might offer further improvements in reducing recombination losses and enhancing the electrical properties of the cells.

TABLE III THE RESULTS OBTAINED BY QSS-SUN V_{oc} for the cells passivated with double-layer SiN_x/SiO_2 and those passivated with single-layer SiN_x

Cells passivation	$V_{oc} (mV)$	FF (%)
SiN _x /SiO ₂	610.1	79.7
SiN _x	601.4	73.2

Table 2, clearly demonstrates that cells passivated with a double SiN_x/SiO_2 layer exhibit a Voc of 610.1 mV with a fill factor of 79.7%, which represents highly promising results in terms of passivation compared with cells passivated with a single SiN_x layer, which have a V_{oc} of 601.4 mV with a FF of 73.2%.

The results obtained by QSS-Sun V_{oc} thus corroborate those obtained by the solar simulator and validate the assumptions made in the explanation of the I (V) characteristics. These assumptions were that the low form factor is due to the existence of a high series resistance.

In view of the results obtained, we can therefore state that the cells developed as part of this project with a SiN_x/SiO_2 double passivation layer offer better electrical performance, due to the field effect passivation (repulsion of charge carriers at the surface) induced by SiO_2 , in addition to the chemical passivation (saturation of dangling bonds) induced by the H-SiN_x layer. These findings can be a promising way for the anti PID phenomenon.

IV. CONCLUSIONS

In the context of the ongoing trend towards thinner and more efficient silicon solar cells, surface passivation is becoming an increasingly significant issue. The abrupt discontinuity in the crystal structure at the crystalline silicon (c-Si) surface results in a high density of dangling bonds, which creates a large density of defects in the bandgap.

The implementation of passivation schemes enables the termination of these dangling bonds in an optimal manner, consequently leading to a notable reduction in the number of recombination centres. Silicon dioxide (SiO₂) and silicon nitride (SiNx) represent the prevailing surface passivation materials. In this study, a combination of these two dielectrics was employed on a standard solar cell Al-BSF, with the objective of investigating the electrical and optical characteristics.

The results obtained using the solar simulator and the Qss-Sun Voc technique demonstrated that superior passivation is achieved with the SiNx/SiO2 double passivation layer. Specifically, we recorded a pseudo-opencircuit voltage (pseudo-Voc) of 610.1 mV and a pseudo-fill factor (pseudo-FF) approaching 80%. This indicates a significant improvement in the electrical performance of the solar cells. Additionally, the optical behavior of devices incorporating the double passivation layer was highly favorable. The reflection was notably minimal at a wavelength of 600 nm, which is crucial for enhancing light absorption and overall efficiency.

This study provides promising prospects for the development and analysis of photovoltaic (PV) modules featuring cells with a SiNx/SiO2 double passivation layer. Such advancements are particularly important for mitigating potential induced degradation (PID), a common issue that leads to the deterioration of PV module performance over time as highlighted by J. Lu et al., So, it is important to address PID phenomenon is essential for ensuring the long-term reliability and efficiency of solar energy systems. Furthermore, the implementation of the SiNx/SiO2 double passivation layer could pave the way for more robust and durable solar cells, potentially leading to broader adoption in commercial PV modules. The enhanced passivation not only improves the initial performance metrics but also contributes to the longevity and stability of the solar cells under various environmental conditions. This research underscores the critical role of advanced passivation techniques in the ongoing quest to optimize solar cell performance and reliability.

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