

Surface passivation layers for multicrystalline silicon solar cells

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Abstract

Both silicon oxide and silicon nitride have the potential to efficiently passivate phosphorus emitters of silicon solar cells. A comparison of the two techniques is carried out in this work for multicrystalline substrates. Optimisation of deposition conditions for silicon nitride by remote PECVD leads to very low surface recombination velocities under 200 cm/s.

1. Introduction

The photovoltaic industry is currently tending towards thinner wafers and higher cell efficiencies. Because of that, the passivation of the front and rear surfaces has an increased importance to reach good characteristics in solar cells.

The surface represents the largest possible disturbance in symmetry of the crystal lattice and hence, due to non saturated bonds, a large density of defects ('surface states') within the bandgap exists at the surface of the crystal. In order to keep surface recombination losses at silicon (Si) surfaces at tolerable levels, they must be electronically well passivated.

Trying to reduce the front surface recombination velocity (SRV), three kinds of surface passivation technologies are going to be studied: thermal oxidation in a conventional diffusion furnace, silicon nitride layers using a remote PECVD with an high excitation frequency, and a double layer of thermal SiO₂ and plasma SiN_x.

Thermally grown silicon oxide films have been studied to passivate silicon surfaces since 1960, allowing the development of integrated circuits [1]. The oxide grows into the wafer by consuming the underlying silicon. Because of that, the oxygen must diffuse through the SiO₂ film and finally it generates a new interface within the wafer. This displacement of the interface to clean regions within the wafer is one of the main reasons for the excellent quality of thermally grown Si-SiO₂ interfaces, which exhibits a few interface state density. On high resistivity silicon (> 100 Ωcm) p-type Si wafers, this method is capable of providing extremely low surface state densities of $\approx 10^9 \text{ cm}^{-2} \text{ eV}^{-1}$ as demonstrated by SRV values below 10 cm s⁻¹ [2]. For

low substrate resistivities ($\approx 1 \text{ Ωcm}$) the passivation quality depends on the doping type: n-Si surfaces can be more efficiently passivated than p-Si ones, but both are poorer [3].

Significant effort has been devoted in recent years trying in to obtain low temperature (<500°C) surface passivation schemes as an alternative to the high temperature oxidation of Si. The most successful of these approaches is Plasma Enhanced Chemical Vapor Deposition (PECVD) of silicon nitride (SiN_x), based in the plasma-enhanced reaction of silane and ammonia mixtures at reduced pressure ($\approx 1 \text{ mbar}$) and temperatures below 500°C [4].

There are two different methods of PECVD SiN_x deposition; direct and remote. In direct PECVD, the wafers are situated at the electrodes which induce the plasma and are thus directly exposed to it. In remote PECVD, the excitation occurs at a separate location and the wafers are situated down stream, thus avoiding any contact with the plasma. Its' main advantages respect the direct PECVD are the higher deposition rate and the absence of silicon surface damage.

PECVD SiN_x has two important additional advantages for Si solar cells. First, its refractive index can be strongly varied and adjusted to give excellent performance as a single or double layer antireflection (AR) coating on both encapsulated and non encapsulated Si cells. Second, PECVD SiN_x contains large amounts of hydrogen. During annealing at temperatures in the 600–800°C range, some of this hydrogen travels into the silicon and is responsible of an improvement to the bulk lifetime [3].

Finally, another possibility to reach a good surface passivation is with a double layer of thermal SiO₂ and PECVD SiN_x. Some researches have concluded that this passivation process increases the thermal stability during subsequently annealing steps [5].

2. Approach

Different experiments have been carried out at our laboratory in order to obtain low surface recombination values on multicrystalline Si substrates. Figure 1 sketches the steps followed.

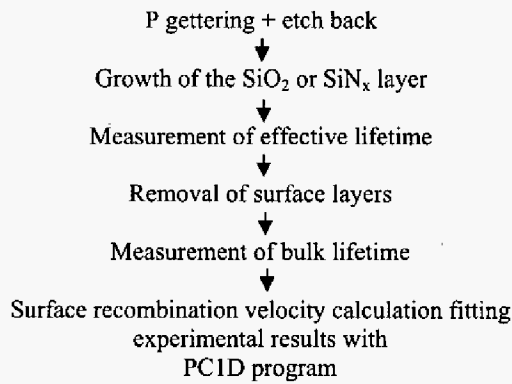


Fig. 1. Measure of the surface recombination velocity

The material used in this work is 1–1.5 Ωcm , p-type multicrystalline silicon (Mc-Si).

Based on parameters measured and deduced from characterization experiments of our Mc-Si material, PC1D simulations shown that the front SRV (S_f) has a relevant role in order to obtain high efficiencies on P/Al Mc-Si solar cells. In figure 2 the efficiency appears as a function of S_f .

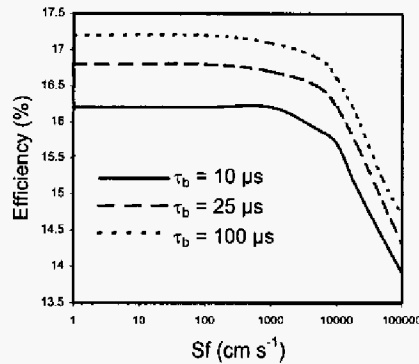


Fig.2. Efficiency of a solar cell as a function of the S_f for bulk lifetimes between 10 μs and 100 μs

To obtain high efficiencies solar cells, values of SRV lower than 5000 cm/s must be reached [6].

Recently a remote PECVD system (model AK400 from Roth & Rau) has been installed at our Institute. Different experiments have been carried out trying to optimise a SiN_x layer in order to reach lower SRV values than with SiO_2 . As seen in Figure 3, higher temperatures result in lower values for the SRV. It was also observed that this gave better uniformity if the SiN_x layer. Figure 4 shows the refraction index and the deposition rate as a function of the SiH_4/NH_3 ratio and based on this information we can obtain different process times and gas flow ratios for optically optimising the SiN_x coating.

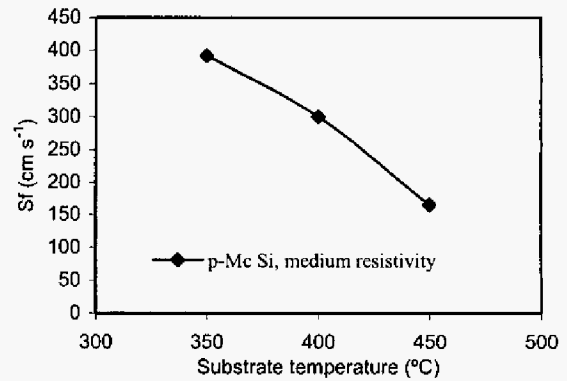


Fig. 3. Surface recombination velocity as a function of the deposition temperature

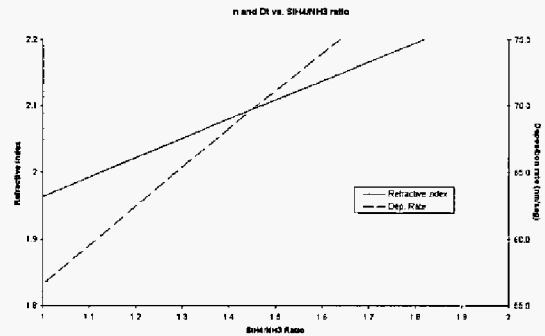


Fig. 4 . Refractive index and deposition rate versus silane-ammonia ratio

The lowest SRV values obtained at the moment for our material with a SiN_x layer is 430 cm/s and 165 cm/s with and without phosphorous emitter, respectively.

3. Application in our solar cell process

P/Al solar cells have obtained nice results for high quality materials (FZ) with a somewhat unsophisticated process [7]. An adaptation of that process to use Mc-Si had been carried out in our laboratory with a reduction of thermal loads. The new process and the lifetime evolution after each thermal step appear in figure 5 and 6 respectively [6].

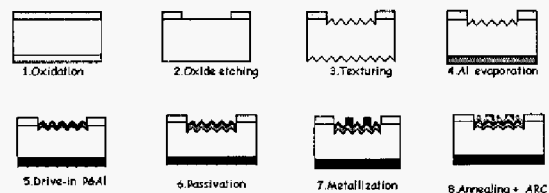


Fig. 5. P/Al cell process for multicrystalline substrates

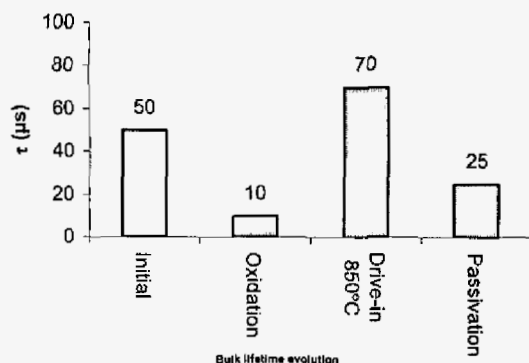


Fig. 6: Bulk lifetime evolution. Injection level $n = 10^{16} \text{ cm}^{-3}$

Initially, a wet and dry oxidation at 1000°C during 3 hours is performed to obtain a thick masking oxide. Then we define the active area window. After the texturization, a $1.5 \mu\text{m}$ thick aluminium layer is evaporated on the rear side. A P/Al co-gettering process follows, with P diffused under super-saturation conditions at 850°C . An etch-back step in HF/HNO_3 solution leads to an increased sheet resistivity (between 80 and $100 \Omega/\square$), etching away the dead layer and most of the gettered impurities. Afterwards a thin oxide is grown at 850°C to passivate the front surface. Front and rear contacts are obtained with evaporation of Ti-Pd-Ag and Al-Ag, respectively, followed by electrolytic growth of the front grid. To improve metal adherence and recover surfaces damaged by electron-gun X-rays, an annealing in forming gas at 450°C is performed. Finally, we grow a double anti-reflecting coating ($\text{ZnS} + \text{MgF}_2$).

It seems P/Al co-gettering easily getters the contamination introduced during the oxidation, but only up to the level allowed by the material quality. Unfortunately, the need of a passivation step reduces final lifetime to the level of $25 \mu\text{s}$.

Figure 2 shows that for that final lifetime and with SRV values higher than 5000 cm/s the efficiency expected is in the range of 14.5 and 16.0% . The results achieved in our best 4 cm^2 solar cell appear in table 1, and are inside that range.

J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	$\eta(\%)$
33.5	611	0.74	15.2

Table1. Parameters of a P/Al solar cell fabricated with the process of figure 5.

In order to reduce the front surface recombination value and increase the final lifetime, we change the SiO_2 for a SiN_x layer during the passivation step. Three different passivation methods were studied: with SiO_2 , with SiO_2 and SiN_x , and with SiN_x . The final lifetimes are shown in figure 7.

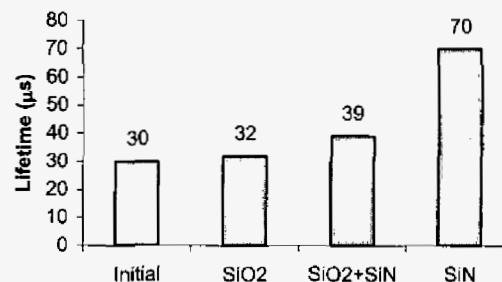


Fig. 7: Final lifetime values. Injection level $n = 10^{16} \text{ cm}^{-3}$

The thermal load associated to the the passivating oxide growth is responsible of the bulk lifetime degradation after the P/Al co-gettering process. For the second and third cases, the hydrogen content in the SiN_x layer can passivate some defects present in the bulk. Using SiO_2 and SiN_x that effect is lower due to the previous growth of a SiO_2 layer at 850°C . Efficiencies higher than 17% are expected in a solar cell with a combination of the lifetimes reached with only the SiN_x layer with low SRV values.

Our first results with the integration of this alternative to the P/Al cogettering process, presented in table 2, has not reached the expected improvement, due to the fact that the SiN_x layer has not been optimised for AR coating conditions.

J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	$\eta(\%)$
29.0	592	0.79	13.5

Table2. Parameters of our best solar cell passivated with SiN_x .

Further work on optimization of SiN_x layer conditions is in progress. Due to the fact that both high final lifetimes, and low surface recombination velocities are achieved with this approach, we expect to obtain high efficiency results in the near future.

4. Conclusions

Thermal loads during a solar cell process are responsible of low final lifetime values. For low quality materials this effect is accentuated. Because of that, a reduction in thermal steps are necessary in order to obtain better solar cells characteristics. Passivation using a SiN_x layer presents several features which make it attractive with low quality materials, like low SRV values and low process temperatures ($\leq 450^\circ\text{C}$).

The improvement in surface passivation with SiN_x as compared to SiO_2 has been experimentally verified. At the moment, efficiencies achieved with the SiN_x layer are lower than those obtained with SiO_2 . Further optimisation work needs to be done. PC1D simulations shows that combining the effect of high final lifetimes and low front SRV, efficiencies higher

than 17% can be achieved in Mc-Si material.

5. Acknowledgements

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