DRY PHOSPHORUS SILICATE GLASS ETCHING FOR CRYSTALLINE SI SOLAR CELLS

Rentsch, J.[1], Binaie, F.[1], Schetter, C.[1], Schlemm, H.[2], Roth, K.[2], Theirich, D.[3], Preu, R.[1]
[1]Fraunhofer ISE, Heidenhofstr. 5, 79110 Freiburg, Germany
Phone +49-761-4588-5199; Fax +49-761-4588-9250; email: jochen.rentsch@ise.fraunhofer.de
[2]Roth & Rau AG, Gewerbering 10, 09337 Hohenstein-Ernstthal, Germany
[3]fmt, Obere Lichtenplatzer Str. 336, 42287 Wuppertal, Germany

ABSTRACT: Dry plasma etching techniques could be of permanent importance in future complete in-line fabrication of crystalline silicon solar cells. Phosphorus silicate glass (PSG) etching represents the most challenging process step, since it has to be etched fast and residual free, without damaging the underlying emitter layer. In this paper we present a process sequence which meets all this requirements. With different CF-containing etch gas mixtures high SiO_2 to Si selectivities together with high etch rates could be reached enabling short process times. A plasma post cleaning step ensures a clean and well conditioned surface for the subsequent SiN_x deposition. Dry PSG etched solar cells reached efficiencies of 14.6 % on mc-Si and 15 % on Cz-Si, having similar or even better performance in all solar cell parameters compared to wet chemically PSG etched reference cells. Upscaling of the selective etching processes to an industrially suitable in-line etching system with high wafer throughput has been successfully demonstrated.
Keywords: Silicon, Manufacturing and Processing, Etching

1 INTRODUCTION

Thinking about common fabrication lines in solar cell production, wet chemical phosphorus silicate glass (PSG) removal represents a process step with a high degree of automation and wafer handling. Recently, wet chemically in-line etching systems represent certain progress in reducing wafer handling steps, but still these processes are characterised by high water and chemical waste disposal as well as high mechanical impact. Therefore, for complete in-line production of solar cells dry PSG plasma etching represents the most favorable solution [1,2]. Main advantage of this approach is the possibility of an integrated etching and deposition process equipment without breaking vacuum. Furthermore, during dry processing full control of all process parameters is possible allowing good reliability and reproducibility, that is necessary for industrial production.

From semiconductor industry, selective etching processes with carbon-fluoride containing etching gases are well known for many years [3]. Unfortunately, demands for solar cell production differ significantly. Enabling a high wafer throughput, the etching processes have to be very fast, but still overetching and therefore damaging of the solar cells emitter layer has to be avoided.

The aim of this work is the development and implementation of PSG plasma etching processes for in-line production in solar cell fabrication. Process development has been performed on a single wafer laboratory etching reactor. To achieve the goal of high wafer throughput different types of plasma sources and etch gases suitable for high etch rates and selectivity are transferred to an in-line capable industrial plasma etching system.

2 EXPERIMENTAL

Experiments concerning PSG removal were carried out on a so called ECR-RIE plasma system. A microwave powered electron cycloton resonance (ECR) plasma source on top of the reaction chamber provides a high density plasma, additionally or alternatively, the sample electrode can be powered by radio frequency to accelerate (reactive) ions onto the sample (RIE / MWRIE mode). Details of the system setup are described elsewhere [2]. The optimization of etching processes with high selectivity between $POCl_3$ based PSG and the underlying silicon emitter layer has been carried out using different carbon-fluoride based source gas mixtures (C_4F_8/O_2, CHF_3/O_2, CF_4/C_2H_4).

Main focus has been put on significant etch rates, selectivity, process stability and homogeneity. Thermally grown SiO_2 served as a substitute for PSG during process development since it has very similar etching properties. Silicon etch rates are determined by measuring the emitter sheet resistivity on $POCl_3$ diffused Si-wafers before and after etching. Different gas mixtures have been tested for a subsequent plasma cleaning step after PSG etching. Criteria of choice was the residual removal efficiency determined by x-ray photoelectron spectroscopy (XPS).

Upscaling of selective etching processes to an in-line capable industrial plasma etching system suitable for high wafer throughput (see Fig. 1) has been undertaken using two different plasma source types: a hollow cathode (HCD) plasma source and a low frequency (LF) linear plasma source. Results regarding the linear plasma sources are also presented by K. Roth et. al. at this conference.

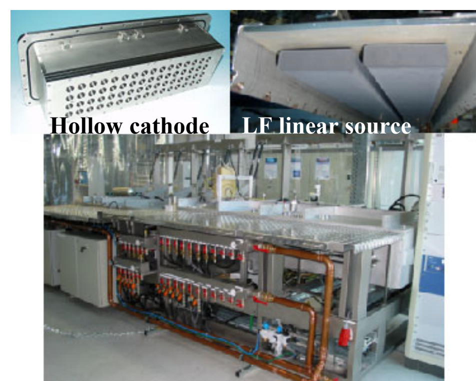

Fig. 1: In-line plasma etching system with low frequency (LF) linear plasma source and hollow cathode (HCD) plasma source.

The working principle of the HCD plasma source is the hollow cathode effect. Cylindrical hollow cathodes are arranged in a hexagonal matrix building the basic plasma. The cathodes are coupled with a high frequency (HF) generator. At the bottom side (anode) openings in the same hexagonal matrix order provide the extraction of intensive plasma jets out of the cathode cylinders.The LF linear plasma source is characterised by two graphite electrodes. Power to both electrodes is supplied by a low frequency generator with a working frequency of around 110 kHz. The source generates a quite high ion current density and is therefore in principal suitable for oxide etching.

2.2 Solar cell processing

Multicrystalline (mc) and Czrochalski (Cz) grown silicon wafers (size: 100 cm², p-type, 0.5 – 2 Ωcm) have been used for solar cell manufacturing. The full process sequence is shown elsewhere [2]. Different to conventional industrial solar cell production processes, wet chemical removal of PSG has been replaced by an optimized plasma process described below. Also, the solar cells contacts have been fired using Rapid Thermal Firing technique in a single-wafer RTP furnace [4]. In the end edge isolation has been carried out using a Nd:YAG laser system.

3 RESULTS

3.1 Selective etching of SiO_2/PSG over silicon

Commonly used for selective etching of SiO_2 over silicon in semiconductor industry are mainly carbon-fluoride containing etching gases [3]. In our study, results are presented for the etchgas mixtures C_4F_8 / O_2, CF_4 / C_2H_4 and CHF_3 / O_2. Because of the chemical inertness of SiO_2, significant ion energies, e.g. applied bias voltages, are required to etch SiO_2 layers at an accetable rate (see Fig. 2). For high ion energies, physical sputtering is an important erosion mechanisms and it becomes difficult to stop etching on a chemically different material.

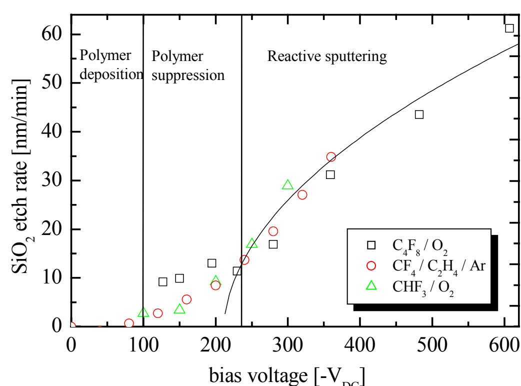

Fig. 2: SiO_2 etch rates versus applied bias voltage for the different gas mixtures. Indicated by the vertical lines are the different plasma etch regimes.

An adequate etching selectivity of SiO_2 with respect to the underlying silicon emitter can be only achieved by covering the underlayer with a thin steady-state polymer layer to prevent ion-induced etching.

Using fluorine-deficient polymerizing fluorocarbon plasmas, e.g. CHF_3, CF_4 and C_4F_8 with small amounts of additive gases, e.g. ethylene (C_2H_4) [5], oxygen and/or argon and a sufficiently enough bias voltage are applied to the wafer, a complex balance among fluorocarbon deposition, fluorocarbon etching and substrate etching produces a thin fluorocarbon film on the substrate surface [6,7]. The chemical differences between SiO_2 and silicon allow for a window of selective etching since the balance for one material can favor etching while for the other material it can tend towards deposition (Fig. 3). Depending on the applied bias voltage, for all etch gas mixtures a SiO_2 to Si selectivity of more than 3 can be achieved, meaning selectivities of PSG to Si in the range of 8-10 since the etch rate in PSG is typically a factor of 2.5 higher than the etch rate for SiO_2 [2].

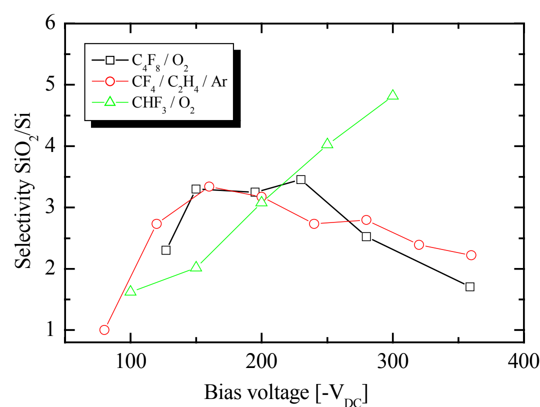

Fig. 3: SiO_2 to silicon selectivity for different etch gas mixtures versus the applied bias voltage.

3.2 Removal of polymer residues

Although high ion energies are involved during the etching process, the emitter layer is always protected against ion induced damage due to the formation of the steady-state fluorocarbon layer. Though this layer has to be removed prior to further solar cell processing, since it causes problems during contacting and changes the properties of the antireflection coating. Different plasma post cleaning procedures have been applied varying the etch gas composition.

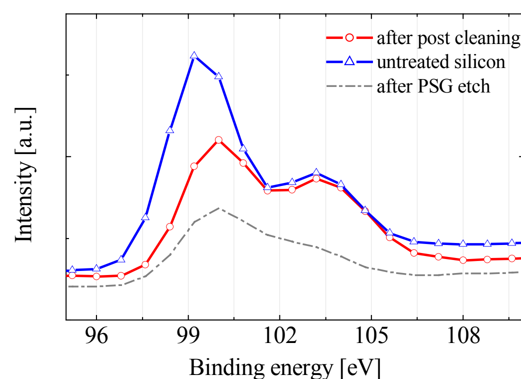

Fig. 4: XPS Si(2p) spectra of Plasma-PSG etched wafers before and after different post plasma cleaning steps.

XPS Si(2p) electron emission spectra shows, that with a

suitable post plasma treatment polymer film can be efficiently removed.

Compared to the surface state directly after the selective PSG etch step, both the elemental Si peak at approximately 99.5 eV as well as the higher binding energy peak at 103 eV corresponding to oxygen bonding to silicon are mostly recovered to their untreated surface state indicating a sufficient surface cleaning.

3.3 Solar cell results

Table 1 shows the results of solar cells with dry etching of PSG in comparison to wet chemically processed references on untextured Cz- and mc-silicon material. Listed are best cell results as well as mean cell results of at least 5 solar cells. Best solar cell results have been reached with the dry PSG etch sequence resulting in 14.6 % efficiency on mc-Si and 15 % efficiency on Cz-Si material. As a result of the successfully implemented plasma post cleaning step, short circuit currents of the dry PSG etched cells are comparable or even better than the wet chemically etched references.

Table 1. Results of untextured solar cells on p-type Cz- and mc-Si material (total cell area 96.1 cm²).

	V_{oc} [mV]	j_{sc} [mA/cm²]	FF [%]	η [%]
mc-Si, dry PSG etched				
best cell	612	30.9	77.2	14.6
mean	608 ± 2	30.1 ± 0.4	77.7 ± 1.0	14.3 ± 0.3
mc-Si, wet chemical references				
best cell	611	30.1	79.0	14.5
mean	612 ± 1	29.8 ± 0.5	77.8 ± 1.0	14.2 ± 0.2
Cz-Si, dry PSG etched				
best cell	617	30.4	80.0	15.0
mean	617 ± 1	30.4 ± 0.2	78.7 ± 0.9	14.8 ± 0.2
Cz-Si, wet chemical references				
best cell	619	30.8	77.6	14.8
mean	616 ± 2	30.6 ± 0.4	78.2 ± 2.0	14.7 ± 0.2

Plasma-induced damage of the wafers due to the high ion energies applied can be neglected, since open circuit voltages of the dry etched wafers are also comparable to their wet chemical references.

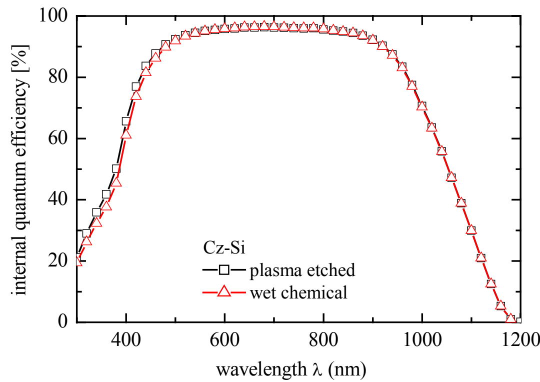

Fig. 5: Internal quantum efficiency of Plasma PSG etched and cleaned Cz-Si solar cells in comparison to a wet chemically processed reference cell.

Further prove of the successful etching procedure gives an internal quantum efficiency measurement, as shown in Fig. 5 for solar cells on Cz-Si material. Almost no difference can be seen between the plasma PSG and the wet chemically etched solar cell. The improved IQE for small wavelength for the dry etched cell may be attributed to a slightly higher sheet resistance of the emitter layer.

Calculating the effective diffusion length from the inverse IQE, the results in Table 2 show always higher values for the dry etched solar cells compared to the wet chemical references indicating a high bulk passivation quality.

Table 2: Calculated effective diffusion length L_{eff} for dry and wet PSG etched solar cells for both material types.

Material	Process	L_{eff} [µm]
Cz-Si	dry	393
	wet	379
mc-Si	dry	420
	wet	230

3.4 Upscaling of selective etching processes to industrial inline etching equipment

For a successful implementation of the dry PSG etching process in an industrial production environment, the etch process has to be transferred to an industrial suitable in-line etching system. A picture of the system developed by Roth&Rau is shown above and will be thoroughly discussed in the contribution of K. Roth et. al. at this conference.

Main challenge in upscaling selective etching processes to large areas is the maintenance of a high ion energy over the whole area without directly applying a bias voltage to the moving carrier. Two different plasma source types with a width of more than 80 cm suitable for homogeneous etching have been investigated, a hollow cathode and a low frequency linear plasma source.

For the selective removal of SiO_2 over Si a different gas mixture has been chosen, CF_4 and H_2, because additional carbon is added to the plasma due to a carbon containing carrier material. In Fig. 6, etch rates of SiO_2 and Si and the corresponding selectivity is shown in case of the low frequency (LF) linear plasma source in dependence of the applied LF power.

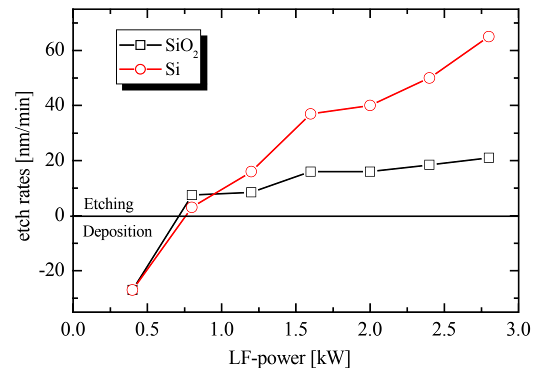

Fig. 6: SiO_2 and silicon etch rates as a function of applied LF power for CF_4/H_2 plasma. Overall etching starts above a certain minimum power level.

Similar to the behavior of the single wafer ECR-RIE system, a certain LF power is necessary to prevent polymer deposition and to start etching.

The second important process parameter controlling selectivity is the process pressure as can be seen in Fig. 7. With increasing pressure the etch selectivity can be slightly improved, but still on a very low level. In addition the SiO_2 etch rate drops below 10 nm/min for pressures above 0.2 mbar, but high SiO_2, e.g. PSG etch rates are necessary to allow the demanded wafer througput.

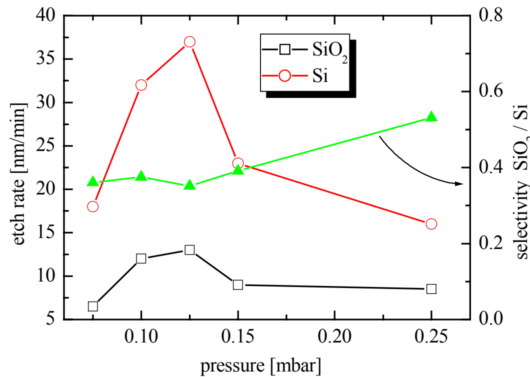

Fig. 7: SiO_2 and silicon etch rates and corresponding selectivity in dependence of the process pressure during CF_4 / H_2 etching with the LF plasma source.

In case of the hollow cathode plasma source, SiO_2 and silicon etch rates reach similar values as for the LF plasma source, overall etch rates decrease for higher process pressure. A different behaviour shows the etch selectivity, for low pressures SiO_2 to Si selectivity increases even without H_2 incorporated, independently of the total gas flow.

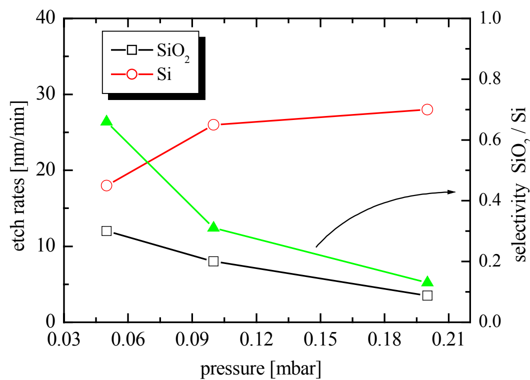

Fig. 8: SiO_2 and Si etch rates and corresponding selectivity in dependence of the process pressure for a CF_4/Ar plasma during etching with the hollow cathode

Therefore to allow reliable PSG removal for solar cell processing in an inline capable system without high etch selectivity, etch stop to the emitter layer can also be realized by an exact adjustment of the carrier moving velocity. By this method overetching of the solar cells emitter can be reduced to a few nanometers. Although, for an advanced process stability and reliability, etch selectivity will be necessary compensating varying process conditions, e.g. varying PSG thickness.

4 CONCLUSION

The suitability of dry etching techniques for the selective removal of PSG in solar cell fabrication has been demonstrated on a single wafer ECR-RIE etching system. For a couple of etch gas mixtures, selectivities between SiO_2 and Si of more than 3 have been reached. Due to a steady state polymer layer enabling high selectivities, an additional polymer removal etching step has been implemented ensuring high surface quality prior to the SiN_x deposition. Solar cells, processed with the dry etching steps, reached similar or even slightly better efficiencies than wet chemically etched references. Upscaling of the etching processes to an industrial suitable inline etching system has been undertaken, a hollow cathode and a LF linear plasma source showed their potential for the transfer of the selective etching processes. Due to the lack of additional substrate biasing, achieved etch rates and selectivities did not reach the values of the single wafer system, but due to the non static etching process, short term lower selectivities can be compensated by the carrier moving velocity. Further development towards higher etch selectivities will secure process stability in the future.

5 ACKNOWLEDGEMENTS

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