

HYDROGEN PASSIVATION AND SILICON NITRIDE DEPOSITION USING AN INTEGRATED LPCVD PROCESS

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ABSTRACT. Hydrogen passivation and low pressure chemical vapour deposition (LPCVD) of silicon nitride (SiN_x) have been efficiently combined in a hot-wall reactor. Atomic hydrogen is generated in a microwave-induced remote plasma from either ammonia or He/H_2 gas mixture. The improvements achieved on multicrystalline material are significant. By applying hydrogen passivation, the effective minority carrier lifetime can be doubled with respect to standard LPCVD silicon nitride. Processed solar cells show a relative improvement of 5.7%. Most standard LPCVD reactors can easily be upgraded with the H-passivation option without any or only a small prolongation of process time.

Keywords: Passivation – 1: Silicon-Nitride – 2: Lifetime – 3

1. INTRODUCTION

At the moment, the commonly used antireflection coatings of industrial solar cells consist of titanium dioxide (TiO_2) or silicon nitride (SiN_x). Silicon nitride can be deposited either by plasma enhanced chemical vapour deposition (PECVD) or low pressure chemical vapour deposition (LPCVD). Low pressure chemical vapour deposition of silicon nitride is a proven technology in microelectronic device fabrication with many advantages such as excellent homogeneity, simple wafer handling and reasonable costs of the apparatus. Standard LPCVD silicon nitride has hydrogen concentrations of below 3 at.% [1], whereas in PECVD silicon nitride H-concentrations up to 25 at.% have been achieved [2]. Especially for multicrystalline silicon solar cells, effective hydrogen passivation is needed and should be applied as simply as possible. TiO_2 -layers contain no hydrogen, therefore the solar cells have to be passivated in an extra step [3]. This extra step can be integrated in an LPCVD silicon nitride process without further complications [4]. The integration of hydrogen passivation into the LPCVD process does not affect silicon nitride deposition and is therefore easily adjustable to any type of silicon material, whereas hydrogen passivation and optical properties of PECVD silicon nitride cannot be separated.

2. PROCESSING

2.1 Reactor set-up

Fig. 1 shows the LPCVD Reactor, a commercially available system with a modified quartz vacuum tube, which allows atomic hydrogen to be generated and let in at either the pumping or loading side. Injection of hydrogen from the pumping side turned out to be not favourable, as a sufficiently uniform distribution of atomic hydrogen could not be achieved. For this reason the hydrogen injection from the pumping side was not further pursued. For the injection from the loading side, the atomic hydrogen has to travel less than 50 cm until reaching the wafers, without them being exposed to plasma UV radiation.

2.2 Process sequence

Fig. 2 illustrates the elaborated process sequences. The process steps on the middle axis are identical for standard LPCVD and LPCVD+H SiN_x , whereas the different process steps are drawn on the lhs. and rhs. of Fig. 2.

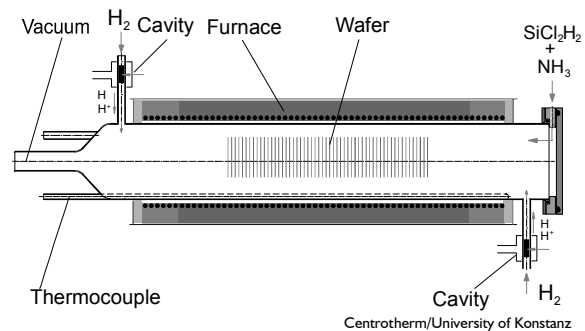


Fig. 1: Schematic view of our LPCVD Reactor, showing the two possible injection modes for atomic hydrogen. The reactive process gases are kept separately until entering the reactor vacuum tube. This reactor design has been applied for patent at the German Patent Office [4].

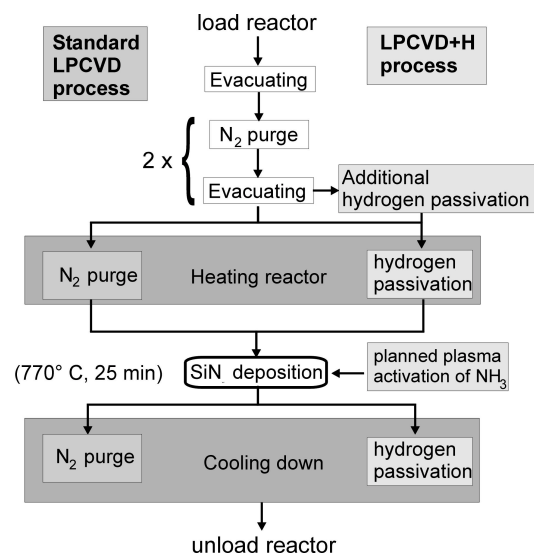


Fig. 2: Flow chart of the LPCVD silicon nitride process sequence. The effect of hydrogen passivation depends on flushing time and temperature ramps. The plasma activation of ammonia has not yet sufficiently been tested.

Hydrogen passivation time while performing temperature ramps is at least 50 min., i.e. no prolongation with respect to the standard LPCVD process. If desired, additional hydrogen passivation can be applied before heating up the reactor. Silicon nitride is deposited using ammonia and dichlorosilane (SiH_2Cl_2) at 770°C and 250 mTorr. With these parameters the SiN_x deposition rate is $27.5 \pm 0.5 \text{ \AA}/\text{min}$ depending on wafer position and total number of wafers per run. The optional plasma activation of ammonia increases has not sufficiently been tested yet, so that all LPCVD SiN_x -layers described in this paper are thermally grown according to the reaction kinetics discussed in [5].

The use of SiH_2Cl_2 leads to NH_4Cl -formation during nitride deposition. NH_4Cl is an unwanted by-product, a white powder which soils vacuum tubes when condensing in cooler areas of a conventional reactor [6]. The newly designed LPCVD+H reactor [4] has no such problems, since all the piping is heated until reaching the cooled reactant gas absorber, which maybe cleaned within ten minutes.

2.3 Reactor capacity

At the moment our reactor is equipped with one 300 mm quartz boat with 120 places for wafers up to $125 \times 125 \text{ mm}^2$, minimum wafer spacing is 2.38 mm, which is sufficient for standard LPCVD processes. If applying hydrogen passivation, wafer spacing should be twice as large. For conventional solar cell fabrication, silicon nitride has to be deposited on only one side of the wafers, so two wafers are set back-to-back and share one boat position. In this way the reactor has a capacity of 120 wafers per run. Batches of up to 40 wafers processed at a wafer spacing of 4.76 mm with the result that effective lifetime values differed less than 10% from the first to the last wafer in the boat.

3. CHARACTERIZATION

3.1 Wafer preparation for lifetime tests

Neighbouring multicrystalline Baysix wafers were submitted to saw damage etching in 25 % NaOH and industrial wafer cleaning in concentrated HCl and diluted HF.

The first group (5 samples, group A) has been processed with LPCVD+H silicon nitride (80 min. total passivation time) and heating temperature ramps of $10^\circ\text{C}/\text{min}$, $12^\circ\text{C}/\text{min}$, $15^\circ\text{C}/\text{min}$ and $700^\circ\text{C}/\text{min}$ (loading at process temperature), plus one reference with standard LPCVD SiN_x with a heating temperature ramp of $12^\circ\text{C}/\text{min}$. Cooling temperature ramp was $10^\circ\text{C}/\text{min}$ for all processes except when loading at process temperature.

The second group (2 samples, group B) was submitted to an emitter diffusion resulting in a sheet resistance of 35 Ohms/sq. After removal of the phosphorous glass, the wafers were covered with LPCVD+H silicon nitride. For heating a temperature ramp of $12^\circ\text{C}/\text{min}$ and passivation times of 110 min. and 170 min have been used.

The third group (12 samples, group C) was also submitted to the emitter diffusion process, but afterwards the emitter has been removed with NaOH followed by industrial wafer cleaning. Then the wafers were covered with LPCVD+H SiN_x with fixed heating temperature ramps of $12^\circ\text{C}/\text{min}$ and various hydrogen passivation times

(50, 80, 110, 170 min.), plus two references with standard LPCVD silicon nitride. The hydrogen passivation times of the LPCVD+H process consist of the times for heating and cooling down the reactor (for a heating ramp of $12^\circ\text{C}/\text{min}$ this results in a minimum of 50 min.) and the additional H-passivation time before heating the reactor.

3.2 Lifetime measurements

Spatially resolved lifetime scans were performed using a microwave-detected photoconductance decay ($\mu\text{-PCD}$) lifetime measurement system. The samples used for measurement were $10 \times 10 \text{ cm}^2$ multicrystalline Baysix wafers (0,5-1,5 Ωcm p-type) treated as described above. Silicon nitride was deposited on the front and back side of the wafers at identical pressures and wafer spacings, but various temperature ramps and H-passivation times.

To obtain the lifetime value at cell operating conditions, the measurement was carried out using $100 \text{ mW}\cdot\text{cm}^{-2}$ biaslight. The laser intensity was set to $2 \cdot 10^{12} \text{ Photons}/\text{cm}^2$ per pulse, leading to minority carrier disturbance of $\Delta n \approx 6 \cdot 10^{14} \text{ cm}^{-3}$. With these parameters an 1 Ωcm wafer is measured under low injection conditions.

Table I: Effect of heating temperature ramps on effective lifetime of wafers with LPCVD+H silicon nitride.

Ramp [K/min]	10	12	15	700
Lifetime [μs]	4.4	6.0	6.5	5.4

The samples with LPCVD+H SiN_x deposited on the emitter (group B) reached an effective lifetime of $10.8 \mu\text{s}$ independent on the H-passivation time.

The samples of group C reached average lifetime values of $1.4 \mu\text{s}$ without and $2.6 \mu\text{s}$ with hydrogen passivation (see Table II). The latter corresponds to an increase of the minority carrier diffusion length of 39 %, but is significant below the lifetimes achieved in group A. As the wafers turned out to be sensitive to temperature ramps, it is necessary to optimise both emitter diffusion and silicon nitride deposition process simultaneously to achieve reasonable lifetime values. This will be subject to further investigations. The deteriorating influence of temperature ramps does not come along with PECVD silicon nitride, as deposition temperatures are much lower (450°C max.). The important result from group C is that the shortest possible hydrogen passivation time (only during temperature ramps) leads to nearly doubled effective lifetime values. This LPCVD+H process does not need more time than the standard LPCVD process.

Table II: Total hydrogen passivation time and measured effective lifetime of LPCVD SiN_x on wafers with removed emitter. The shortest possible passivation time is 50 min. This LPCVD+H process equals the standard LPCVD process in time.

H-passivation Time [min]	0	50	80	110	170
Lifetime [μs]	1.4	2.6	2.6	2.9	2.5

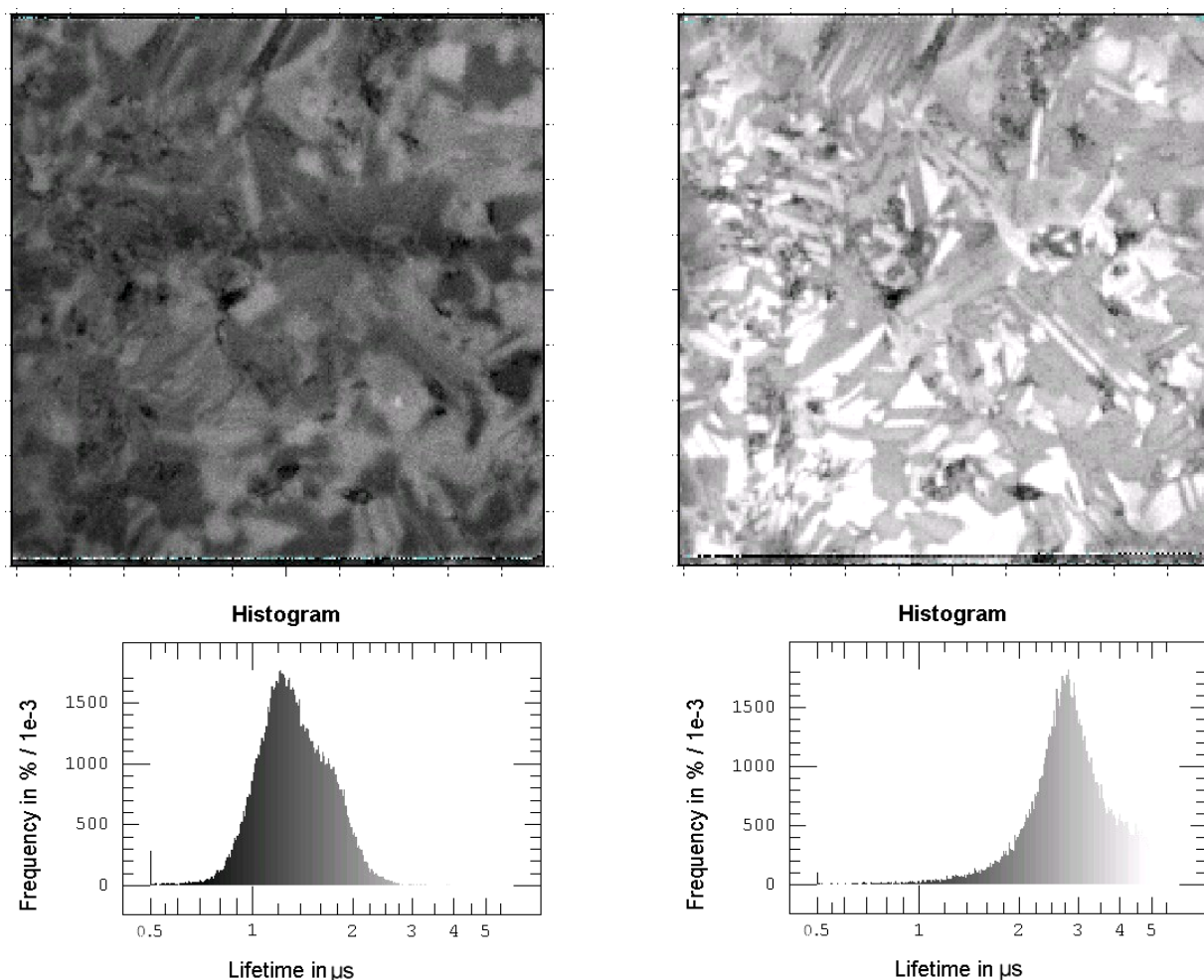


Fig. 3: Lifetime maps of $10 \times 10 \text{ cm}^2$ wafers with standard LPCVD silicon nitride (left) and with LPCVD+H silicon nitride (right). These wafers were submitted to emitter diffusion, then the emitter was removed. The average lifetime is $1.39 \mu\text{s}$ without and $3.18 \mu\text{s}$ with hydrogen passivation

3.3 Optical characterisation

Ellipsometric measurements on polished FZ wafers were performed using a SOPRA ES4G spectroscopic ellipsometer. The wafers were placed at the ends, the middle and random positions of the boat to investigate the homogeneity of the silicon nitride deposition. The ellipsometric data $\tan \psi$ and $\cos \Delta$ were taken over a wavelength range from 390 nm to 890 nm. The film thickness d is determined assuming $k=0$ at 890 nm. Based on this d -value, the optical constants n and k have been calculated in the full wavelength range. For better comparison of the LPCVD silicon nitride with standard PECVD SiN_x films, their stoichiometry has been analysed. The silicon nitride films are assumed to consist of Si_3N_4 , poly-Si and voids [7], each with known n and k -values. Using the Bruggemann Effective Medium Approximation [8], the ϵ -functions of Si_3N_4 , poly-Si and voids are mixed to achieve best agreement with measurement. As a result, LPCVD silicon nitride seems to contain no voids or poly-Si, whereas our PECVD silicon nitride (optimised for best antireflection properties) includes 1%-5% poly-Si and 0%-10% voids depending on deposition parameters.

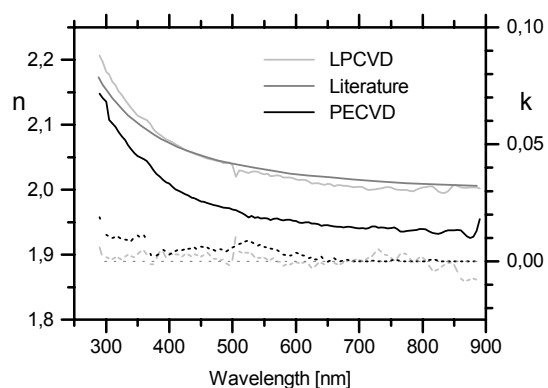


Fig. 4: Measured values of n (straight lines) and k (dashed lines) for LPCVD and PECVD nitride layers compared with literature [9].

According to [2], PECVD silicon nitride contains up to 25 at.% hydrogen. This hydrogen is loosely bound by Si—H or N—H-bonds [1]. The hydrogen of both silicon nitrides is partially released during firing-through-process and may lead to blistering effects [10] of PECVD silicon

nitride films, which was never observed on LPCVD silicon nitride. The hydrogen content of LPCVD silicon nitride films is below 3 at.% [1] and is neglectable for optical properties.

3.4 IV analysis of solar cells

Solar cells were fabricated out of multicrystalline Baysix wafers (0.5-1.5 Ωcm p-type) with an industrial type 30 Ohms/sq. emitter. The optimum firing-through parameters of LPCVD and LPCVD+H SiN_x turned out to be identical and are almost the same as for our PECVD silicon nitride. The cell results from Table III show a relative improvement in cell performance of 5.7 % when using hydrogen passivation. This is consistent with lifetime measurements, when considering that hydrogen passivation improves solar cell performance preferably in the long wavelength range and that the generated photocurrent is governed by the minority carrier diffusion length.

Table III : Averaged IV-results of each five $10 \times 10 \text{ cm}^2$ mc solar cells with optimum firing-through parameters. The wafers were from the same lot, but not neighbouring. The LPCVD+H process was performed with 30 min. additional H-passivation.

Process	FF (%)	I_{sc} ($\text{mA} \cdot \text{cm}^{-2}$)	V_{oc} (mV)	η (%)
Standard LPCVD	76.0	28.6	597	13.0
LPCVD+H	75.5	30.3	599	13.7

3.5 LBIC analysis of solar cells

Light-beam-induced-current (LBIC) measurements at one wavelength deliver lateral information, where hydrogen passivation actually takes place. Fig. 5 shows a detail of an industrial-type solar cell with standard LPCVD SiN_x . Fig. 6 shows a solar cell processed in the same batch, but covered with LPCVD+H silicon nitride. The pictures shown in Fig. 5 and Fig. 6 are directly comparable, as the wafers are from neighbouring positions in the ingot. Both measurements were performed using a 905 nm GaAs laser diode focused to a laser spot of $10 \mu\text{m}$ FWHM, laser power was set to $1.5 \mu\text{W}$. Hydrogen passivation improves the mean LBIC signal by 5.6 %.

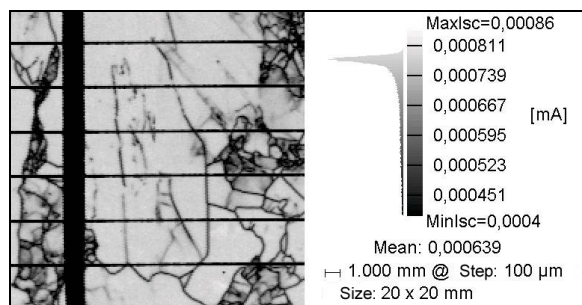


Fig. 5: LBIC scan of a multicrystalline solar cell with standard LPCVD SiN_x (detail of a $10 \times 10 \text{ cm}^2$ cell). This picture is directly comparable with Fig. 6, as the two solar cells were made from neighbouring wafers in the ingot.

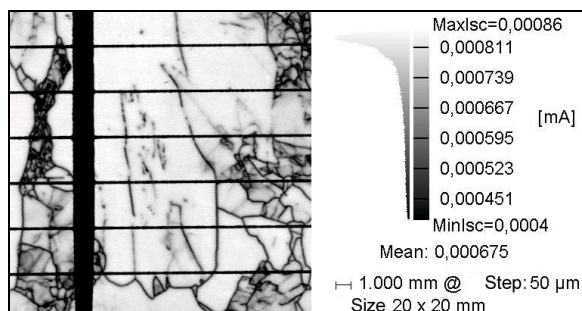


Fig. 6: LBIC scan of a multicrystalline solar cell with LPCVD+H silicon nitride.

4. CONCLUSION

LPCVD silicon nitride in combination with hydrogen passivation is a convenient method to process large charges of wafers. A relative increase in solar cell efficiency of 5.7 % has been achieved on Baysix wafers. The deposited films are of nearly ideal stoichiometry, which creates no problems like blistering with any firing-through process. The equipment necessary for LPCVD silicon nitride deposition is industrial standard with few modifications in hardware for the implementation of the hydrogen passivation. Lifetime measurements demonstrate that an optimised LPCVD+H process does not consume more time than a standard LPCVD process. Some care should be spent on elaboration of optimised emitter diffusion and silicon nitride deposition process sequences, which will be subject to further investigations.

5. ACKNOWLEDGEMENTS

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